Digitized by the Internet Archive
in 2012 with funding from
LYRASIS Members and Sloan Foundation

http://archive.org/details/measurementsofli00tsen

MEASUREMENTS OF LIQUID PHASE DIFFUSION BY THE MICROINTERFEROMETRIC METHOD

by

JIE-TSAI TSENG

B.S., National Taiwan University, 1964

Taipei, Taiwan

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1968

Approved by:

L. I. Stiel

Major Professor

TABLE OF CONTENTS

Chapter		Page
I.	INTRODUCTION	1
II.	THEORY OF DIFFUSION AND PREDICTION OF DIFFUSIVITY	3
III.	EXPERIMENTAL METHOD AND APPARATUS	14
IV.	DIFFUSIVITY OF HONEY-WATER SYSTEM AT 25°C	28
V.	DIFFUSIVITY OF DIETHYLENE GLYCOL-WATER SYSTEM AT 25°C	39
VI.	DIFFUSIVITY OF POLYETHYLENE GLYCOL-WATER SYSTEM AT 25°C	61
VII.	ANALYSIS OF THE RESULTS OF THE FOUR GLYCOL-WATER SYSTEMS AND CONCLUSION	80
	NOMENCLATURE	104
	ACKNOWLEDGMENTS	106
	BIBLIOGRAPHY	107
	APPENDICES	110
I.	SUMMARY OF EXPERIMENTAL DIFFUSIVITY FOR HONEY-WATER SYSTEM AT 25°C	111
II.	SUMMARY OF EXPERIMENTAL DIFFUSIVITY FOR DIETHYLENE GLYCOL-WATER SYSTEM AT 25°C	115
III.	SUMMARY OF EXPERIMENTAL DIFFUSIVITY FOR POLYETHYLENE GLYCOL-WATER SYSTEM AT 25°C	122

LD
2668
T4
1968
T77
C.2

LIST OF TABLES

Table		Page
1.	Viscosities and densities of aqueous honey solutions at 25 °C	29
2.	Refractive indices of aqueous honey solutions at 25 °C	32
3.	Diffusivity of honey-water system at 25 °C	35
4.	D_{AB} of honey in different concentrations	38
5.	Physical Properties of diethylene glycol	41
6.	Viscosities of diethylene glycol solutions at 25 °C	42
7.	Refractive index of diethylene glycol and its aqueous solutions at 25 °C	45
8.	Summary of experimental diffusivities for diethylene glycol-water system at 25 °C	48
9.	Experimental diffusivities and the diffusivities estimated by the Wilke-Chang correlation	55
10.	Comparison of methods of estimating diffusivities in infinitely dilute diethylene glycol-water system at 25 °C	58
11.	Physical properties of commercially available polyethylene glycol	63
12.	Viscosities of polyethylene glycol solutions at 25 °C	64
13.	Refractive index of polyethylene glycol and its aqueous solutions at 25 °C	66
14.	Summary of experimental diffusivities for polyethylene glycol-water system at 25 °C	70

LIST OF TABLES--Continued

Table		Page
15.	Physical properties of the glycols	81
16.	Experimental and calculated values of diffusivity of the infinitely dilute glycol-water systems at 25 °C	94
17.	Summary of experimental diffusivity for honey-water system at 25 °C	110
18.	Summary of experimental diffusivity for diethylene glycol-water system at 25 °C	114
19.	Summary of experimental diffusivity for polyethylene glycol-water system at 25 °C	121

LIST OF FIGURES

Figure		Page
1.	The optical wedge	15
2.	The diagram of the diffusion apparatus	18
3.	The laser light source mounted on the optical bench .	20
4.	The Bausch & Lomb camera and other apparatus for the measurement of the diffusivity of a liquid	21
5.	The diffusion cell on the microstage	22
6.	The coordinate measuring microscope with a photographic plate in position on top of the light box	24
7.	The apparatus assembled for the measurement of the viscosity of a liquid	25
8.	Viscosity vs. concentration for honey-water system at 25 ^{o}C	30
9.	Refractive index vs. concentration for honey-water system at 25 ^{o}C	33
10.	Diffusivity vs. concentration for honey-water and glucose-water systems	36
11.	The D_{AB} vs. concentration for honey-water system .	40
12.	Viscosity vs. concentration for diethylene glycol-water system at 25 ^{o}C	43
13.	Refractive indices vs. concentration for diethylene glycol-water system at 25 ^{o}C	46
14.	Diffusivity vs. concentration for diethylene glycol-water system at 25 ^{o}C	49

LIST OF FIGURES--Continued

Figure		Page
15.	Diffusivity vs. concentration for diethylene glycol water system at 25 °C	50
16.	Diffusivity vs. concentration for diethylene glycol water system at 25 °C	52
17.	D_{AB} vs. concentration for diethylene glycol-water system at 25 °C	53
18.	Diffusivity vs. 1/ for diethylene glycol-water system at 25 °C	56
19.	The deviation of diffusivity from a linear function of mole fraction for aqueous diethylene glycol solutions .	59
20.	Viscosity vs. concentration for polyethylene glycol-water system at 25 °C	65
21.	Refractive index vs. concentration for polyethylene glycol-water system at 25 °C	67
22.	Diffusivity vs. concentration for polyethylene glycol-water system at 25 °C	71
23.	Diffusivity vs. concentration for polyethylene glycol-water system at 25 °C	72
24.	Diffusivity vs. concentration for polyethylene glycol-water system at 25 °C	73
25.	D_{AB} vs. concentration for polyethylene glycol-water system at 25°C	75

LIST OF FIGURES--Continued

Figure		Page
26.	The deviation of diffusivity from a linear function of mole fraction for aqueous polyethylene glycol solution	78
27.	Viscosity vs. concentration for mono, di, tri, and poly-ethylene glycol-water systems at 25 °C	82
28.	Viscosity vs. concentration for glycols-water systems at 25 °C	83
29.	Viscosity of glycol-water systems vs. molecular weight of glycols	85
30.	Refractive indices of aqueous glycol solutions at 25°C	87
31.	Diffusivity vs. concentration for aqueous glycol solutions at 25 °C	88
32.	Diffusivity vs. concentration for aqueous glycol solutions at 25 °C	89
33.	Reference substance plot for the diffusivities of glycol-water system at 25 °C	90
34.	The products of diffusivity and viscosity for aqueous glycol solutions at 25 °C	93
35.	Plot of the Wilke-Chang correlation for ethylene glycol-water system	97
36.	Plot of the Wilke-Chang correlation for diethylene glycol-water system	98

LIST OF FIGURES--Continued

Figure		Page
37.	Plot of the Wilke-Chang correlation for triethylene glycol-water system	99
38.	Diffusivities of glycols and water	100
39.	Diffusivity of ethylene glycol-water system by several workers	102

CHAPTER 1

INTRODUCTION

The diffusion coefficient is a fundamental property which governs the rate of mass transfer. A knowledge of the liquid diffusion coefficient is required for the calculations involved in the design of distillation, extraction, mixing and catalytic reactor systems.

The theory of liquid diffusion is complicated by the fact that no satisfactory theory of the liquid state is available as yet. Most of the available theories on diffusion lack the generality required for their application to a wide variety of systems and concentration ranges. Reported values of diffusion coefficients in the liquid phase are still scarce, especially in concentrated solution; owing to the expensive apparatus and high skill required to obtain them. There is an urgent need for experimental measurements, both for their own value and for the further development of theories.

In recent years, an elegant solution to the problems of measuring diffusion rates has been devised by Yasunori Nishijima of the University of Kyoto in Japan and Gerald Oster of the Polytechnic Institute of Brooklyn (1) in the form of a simple and inexpensive apparatus. The apparatus is as powerful as it is simple. Within minutes, the rate at which diffusion proceeds can be determined.

The present investigation deals with binary molecular diffusion in aqueous systems. In order to study the effect of molecular structure (or molecular weight) on diffusivity, diethylene glycol and polyethylene glycol (average molecular weight 400) have been selected for measurement

since ethylene glycol and triethylene glycol have been already investigated by Jerome (2). Also, in order to study the dependence of binary liquid diffusivity upon concentration, measurements have been made over the fairly broad concentration range at ambient pressure and at a temperature of 25 ^{o}C. To test the adequacy of the apparatus for the measurements of diffusion coefficients of some food stuffs, the diffusivity of honey in water was measured in a high concentration range.

Several empirical correlations are available for the estimation of diffusion coefficients in binary solutions at infinite dilution. In order to test the validity of these empirical correlations, the estimated values are compared with experimental results.

CHAPTER II

THEORY OF DIFFUSION AND PREDICTION OF DIFFUSIVITY

THEORY OF DIFFUSION

In a binary system of two miscible liquids, if inhomogeneities in concentration exist, a driving force is present which tends to make the system homogeneous in the absence of other gradients. This phenomenon is commonly called diffusion. The theoretical foundation of the quantitative study laid by Fick (3) and Graham (4) established the experimental basis. The diffusion coefficient for a simple binary system is defined by Fick's first law. For one dimensional binary diffusion Fick's law may be written as (5)

$$J_A = -C_A D_{AB} \frac{dX_A}{dz} \qquad (1)$$

where J_A (a vector quantity) is the flux or amount of component A passing through a unit area in a reference plane perpendicular to the z direction in a unit time; $\frac{dX_A}{dz}$ is the mole fraction gradient of the component A in the direction of flux; D_{AB} is a proportionality factor called the binary diffusion coefficient. In this relation the assumption is made that D_{AB} is constant for a given system. The negative sign indicates that the flow is toward lower concentration.

Equation 1 is of importance in the study of diffusion by steady state methods in which gradient X_A does not change with time. In most experimental methods currently in use, however, the variation of X_A with both time and distance is studied. To treat the unsteady state diffusion, the equation of continuity of species A is used. Combining it with

equation 1 for the case of constant total density and no chemical reactions gives

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial z}\left(D_{AB}\frac{\partial C_A}{\partial z}\right). \qquad (2)$$

Equation 2 is known as Fick's second law. Provided that equation 2 can be integrated, D_{AB} can be determined from measurements of either $\frac{\partial C_A}{\partial t}$ or C_A as a function of z and t. If the diffusion coefficient, D_{AB}, is a constant, equation 2 becomes

$$\frac{\partial C_A}{\partial t} = D_{AB}\frac{\partial^2 C_A}{\partial z^2}. \qquad (3)$$

If the origin is set at the initial interface, this partial differential equation is solved with the following initial conditions

$$C_A = C'_{Ao} \qquad t=0 \qquad z<0$$

$$C_A = C''_{Ao} \qquad t=0 \qquad z>0.$$

The final form is dependent upon the particular boundary conditions.

1. Free diffusion:

Consider the case where two solutions of different concentration fill a column of effectively infinite length, and the diffusion begins from the sharp interface of the two solutions, i.e., at z=0, or the two solutions fill a finite length column in which concentration changes do not occur at the end of the column during the period of observation; the boundary conditions corresponding to these cases are

$$C_A = C''_{Ao} \qquad t>0 \qquad z = +\infty,$$

$$C_A = C'_{Ao} \qquad t>0 \qquad z = -\infty.$$

The solution of equation 3 has the form

$$C_A = C'_{Ao} - \frac{C'_{Ao} - C''_{Ao}}{2} \left[1 - \text{erf} \left(\frac{Z}{2\sqrt{D_{AB}t}} \right) \right] . \qquad (4)$$

If D_{AB} is to be determined from measurements of the concentration gradient along the column, rather than concentration, it is convenient to use a solution in the form

$$\frac{\partial C_A}{\partial Z} = \frac{C'_{Ao} - C''_{Ao}}{2\sqrt{\pi D_{AB}t}} \exp \left(- \frac{Z^2}{4D_{AB}t} \right) . \qquad (5)$$

Equation 5 is obtained by differentiating equation 4. If a linear relationship exists between the index of refraction n, and the concentration C_A, one can write

$$n = n_o + k\, C_A$$

where n_o and k are constants. Then equation 5 can be written as

$$\frac{\partial n}{\partial Z} = \frac{n''_o - n'_o}{2\sqrt{\pi D_{AB}t}} \exp \left(- \frac{Z^2}{4D_{AB}t} \right) . \qquad (6)$$

This is the desired equation, indicating that from the refractive index gradient one can calculate the diffusion coefficient, D_{AB}.

2. Restricted diffusion:

In a column of finite length, diffusion becomes restricted when concentration changes occur at the ends of the column. The general

solution of equation 3 in the case of restricted diffusion is a Fourier series of the form (6)

$$C_A = A + \sum_{n=0}^{\infty} B_n \exp\left(-\left(\frac{n\pi}{l}\right)^2 D_{AB}t\right) \cos\frac{n\pi z}{l}, \qquad (7)$$

in which A and B_n are coefficients and l is the length of the diffusion column.

In case the diffusion coefficient is regarded as a function of concentration, the basic equation for an unidirectional diffusion at constant temperature is equation 2. Introducing Boltzmann's parameter (7)

$$y = z\sqrt{t}$$

equation 2 is converted into the following ordinary differential equation

$$-\frac{y}{2}\frac{d C_A}{dy} = \frac{d}{d y}\left(D_{AB}\frac{d C_A}{d y}\right). \qquad (8)$$

Integrated once, equation 9 becomes

$$D_{AB} = -\frac{d y}{2d C_A}\int_0^{C_A} y\, dC_A .$$

PREDICTION OF DIFFUSION COEFFICIENT

Prediction of liquid diffusivity is complicated by the fact that no satisfactory theory of the liquid state is available. The existing theories do not provide as good a basis for the prediction of diffusivities as the available empirical equations. Binary diffusion coefficients for dilute solutions may frequently be predicted within 25 per cent. Among the theoretical approaches, the most important ones are the hydrodynamic and Eyring models. In these models, diffusivities are

estimated from more easily measured properties such as viscosity and heat of vaporization.

1. Hydrodynamic theory.

According to Einstein (8) and Smoluchowski (9) the mobility M_{AB} of a single solute molecule of A through a stationary continuum of species B is related to the diffusion coefficient D_{AB} by

$$D_{AB} = M_{AB} k T, \tag{10}$$

where k is the Boltzmann constant and T is the absolute temperature.

Equation 10 is valid for a particle of arbitrary shape as shown by Kuhn (10). The velocity V of a particle is proportional to the affecting force F, that is,

$$V = M_{AB} F . \tag{11}$$

The mobility is calculated by assuming that the particle of A is moving in creeping flow through the continuum of B. Two limiting cases are of interest (5):

(a) "No slip", i.e., the fluid velocity at the surface of the particle equals the particle velocity. Under this condition equation 10 takes the form (5)

$$D_{AB} = \frac{kT}{6 \pi \eta_B r_A} , \tag{12}$$

where η_B is the viscosity of the solvent. This expression has been shown to apply well to the diffusion of very large molecules in low molecular weight solvents.

(b) No momentum flux at the surface of the particle, i.e., there is no tendency for the fluid to stick at the surface of the diffusing particle, equation 10 can be expressed as (5)

$$D_{AB} = \frac{k\,T}{4\,\pi\,\eta_B r_A} \cdot \tag{13}$$

More recently Pyun and Fixman (11) have extended the hydrodynamic theory to systems with concentrations of spherical solutes. For rigid spheres, they show

$$D_{AB} = \frac{k\,T}{6\pi\eta_B r_A}\left(\frac{\partial \ln a_A}{\partial \ln C_A} - 7.16\,\phi_A + O(\phi_A^2)\right) \tag{14}$$

where a_A = activity of the solute

ϕ_A = the solute volume fraction.

Equation 14 reduces to equation 12 at infinite dilution.

2. The Eyring absolute rate theory.

The absolute rate theory is based on a model of a liquid as a quasi-crystalline substance with diffusing molecules "jumping" through ordered layers of solvent molecules.

The original Eyring theory gives a result similar to the hydrodynamic theory (12).

$$D_{AB} = \frac{k\,T}{2\,\eta_B r_A} \tag{15}$$

This has not provided a basis for the reliable quantitative prediction of diffusivities. More recent development, referred to as the "theory of significant structures", re-examines the assumed lattice structure of the liquid and has the following result

$$D_{AB} = \frac{k\,T}{\zeta\,\eta_B (\frac{V_{BO}}{N})^{1/3}} \quad , \tag{16}$$

where ζ = arbitrary packing parameter

V_{BO} = molal volume of solvent

N = Avogadro's number.

Gainer and Metzner (13) propose a different model for the lattice which considers both the intermolecular force field and simple geometric effects to develop expressions for the energy barriers which a diffusing molecule encounters. The diffusivity is found to be

$$D_{AB} = \frac{k\,T}{\zeta\,\eta_B} \left(\frac{N}{V_B}\right)^{1/3} \exp\left(\frac{E_{\eta,B} - E_{D,AB}}{R\,T}\right) , \tag{17}$$

where $E_{\eta,B}$ = energy to overcome viscosity energy barrier

R = gas constant

$E_{D,AB}$ = activation energy for the diffusion process

V_B = molar volume of solvent

The quantity $(E_{\eta,B} - E_{D,AB})$ may be estimated in several ways from heat of vaporization data and from molecular size (13).

3. Statistical mechanical theory.

Rice and coworkers (14-17) derive an equation for the self diffusion coefficient in liquids. Kamal and Canjar (17) have extended the work of Rice and his coworkers to predict the binary diffusivity. They employ intuitional arguments to derive the following equation (17)

$$D_{AB} = 1.2021 \left[\left(\frac{R\,T}{\pi\,M}\right)^{\frac{1}{2}} \left(\frac{V^{1/3}}{v_o/v^{2/3}}\right) 10^{-8} \left\{ 1.6 \left(\frac{v_o}{v}\right) + 2.56 \left(\frac{v_o}{v}\right)^2 g^{(2)}(\sigma) \right\} \right]_{solven}$$

$$\times \left(\frac{R\,T}{24L - 15PV - 15RT}\right)_{solute} \qquad (18)$$

where $\frac{v_o}{v}$ = the ratio between the occupied and total volume per molecule

L = internal energy of the liquid $L = \Delta H_{vap} - RT$

$g^{(2)}(\sigma)$ = correlation function

M = molecular weight

V = molar volume

P = pressure

$\frac{v_o}{v}$ can be calculated from data on the velocity of sound and $g^{(2)}(\ )$ can be approximated by

$$g^{(2)}(\sigma) = 1 + 2.5 \left(\frac{v_o}{v}\right) + 4.5864 \left(\frac{v_o}{v}\right)^2 \qquad (19)$$

4. Empirical correlations.

Based on relations suggested by the Eyring theory and the Stokes-Einstein equation, Wilke (18) has suggested a successful correlation. The Wilke correlation later has been extended by Wilke and Chang (19). The Wilke-Chang correlation can be expressed as

$$D_{AB} = 7.4 \times 10^{-8} \frac{(XM)^{\frac{1}{2}}\,T}{\eta V^{0.6}} \qquad (20)$$

where V = molal volume of solute at normal boiling point, c.c./g-mole

η = viscosity of solution, cp

T = temperature, ^{o}K

X = association parameter.

The values of X, the association parameter, recommended by Wilke and Chang are 2.6 for water; 1.9 for methyl alcohol; 1.5 for ethyl alcohol; 1.0 for benzene; 1.0 for ether and for other unassociated solvents. The molal volume, V, of the solute may be calculated by using the LeBas group contribution method.

Othmer and Thaker (20), employing the analogy between the Eyring theory and Clausius-Clapeyron equation and a variety of experimental data, arrived at the correlation for binary aqueous solution

$$D_{AB} \times 10^5 = \frac{14.0}{\eta_W^{1.1} V_A^{0.6}} \tag{21}$$

where η_W = the viscosity of water

V_A = molal volume of the diffusion substances

For solvents other than water, the following expression was obtained

$$D_{AB} \times 10^5 = \frac{14.0}{\eta_W(1.1 \frac{L}{L_W}) V_A^{0.6} \eta_B^o} \tag{22}$$

where η_B^o = viscosity of solvent at 20°C

L_B, L_W = latent heat of vaporization of the solvent and water respectively.

Sitaraman, Ibrahim and Kuloor, following the earlier development of Ibrahim and Kuloor, developed a general empirical equation (21)

$$D_{AB} = 5.4 \times 10^{-8} \left(\frac{M_B^{\frac{1}{2}} L_B^{\frac{1}{2}} T}{\eta_B V_A^{0.5} L_A^{0.5}}\right)^{0.93} \tag{23}$$

where L_A = latent heat of vaporization of the solute, cal/gram

M_B = molecular weight of solvent.

They claimed that equation 23 is even applicable to the diffusion of water at low concentrations in organic solvents.

In a binary solution at constant temperature and pressure, the dependence of diffusivities on concentration are linear for some systems which are approximately thermodynamically ideal (22). Consequently, it has been assumed (23-25) that the diffusivity which a nonideal system would have if it were ideal varies linearly with the mole fraction between the experimental values of the diffusivity at infinite dilution. That is to say

$$D_{AB}^{o} = D_{B}^{o} X_A + D_{A}^{o} X_B \qquad (24)$$

where D_{AB}^{o} = ideal mutual diffusivity

D_{B}^{o} = mutual diffusivity in an infinite dilute solution of B in A

X_A, X_B= mole fraction of A and B respectively.

The mutual diffusion coefficient is obtained from the ideal diffusivity by multiplying it by a correction term Q as

$$D_{AB}' = D_{AB}^{o} Q \quad . \qquad (25)$$

Based on nonequilibrium thermodynamics, Q has the form (26)

$$\frac{d \ln a}{d \ln x} ,$$

where a is the thermodynamic activity.

MaCall and Anderson (40) have given the following form for the correction

$$Q = \frac{\eta}{\eta_A X_A + \eta_B X_B}, \qquad (26)$$

where η = the viscosity of the solution, cp

η_A, η_B = the viscosities of the A, B components respectively, cp.

The combination of equations 24, 25, and 26 yields

$$D_{AB} = (D_B^o X_A + D_A^o X_B) \frac{\eta}{\eta_A X_A + \eta_B X_B} \qquad (27)$$

This equation may be regarded as the simplest empirical mixture formula.

CHAPTER III

EXPERIMENTAL METHOD AND APPARATUS

THE MICROINTERFEROMETRIC METHOD

As early as 1925, Fürth (27) described a micro-diffusion apparatus. In this early work, diffusion coefficients of two systems were determined by observing the diffusion process through a microscope.

According to the Brownian movement theory the average of the square of the displacement of a particle (or a molecule) is proportional to the time of observation. By observing the diffusion process under a microscope over a small distance, the time required for the observation can be reduced by the square of the magnification factor and measurements in experiments normally requiring one day may take only several minutes to several hours under the microscope.

Light interference methods are particularly suitable for the measurement of refractive index and thereby of concentration. One such method is employed in the present work. It is similar to the method used by Berg (28) for studying concentration profiles around growing crystals.

When a beam of light passes through a wedge of air or of liquids between two partially reflecting glass plates, multiple reflections occur within the wedge and Fabry-Perot type interference fringes are produced. The theory of the formation of the fringes in the wedge is complicated (29). The principle on which the experimental measurements are based can be simply illustrated by Figure 1. A ray of monochromatic light AB, which enters the wedge, is partly transmitted and partly reflected. The reflected ray travels along the path BCD. When the optical path between

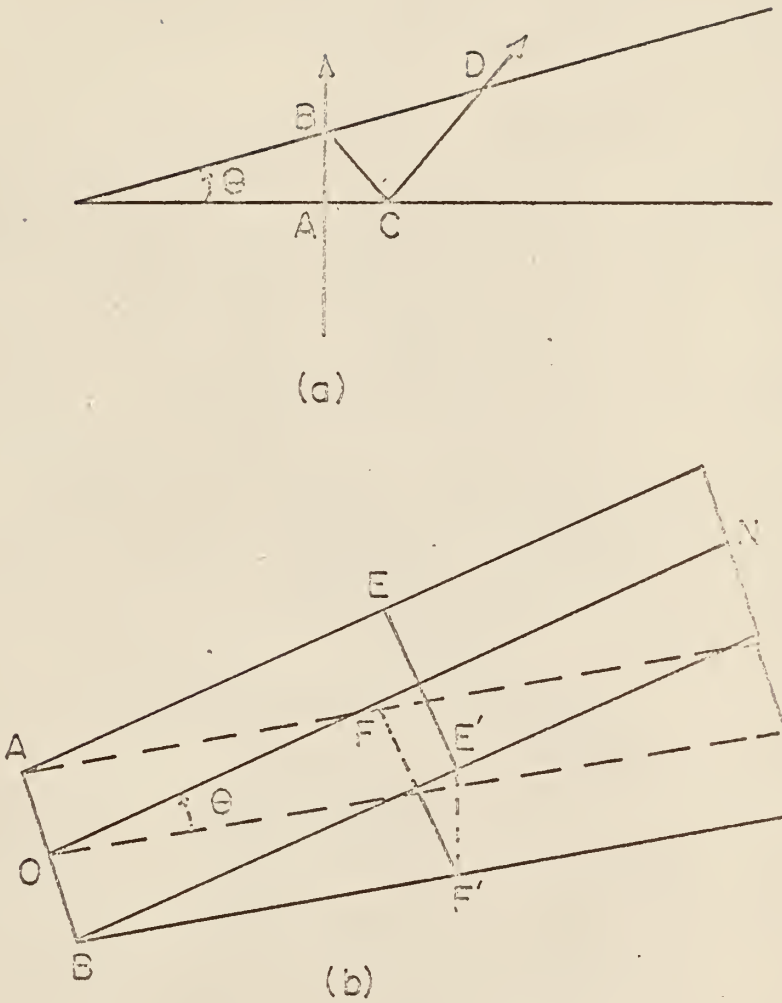


Figure 1. The optical wedge

the reflected and transmitted rays is an integral number of wave lengths, reinforcement occurs and a bright fringe is observed. The optical path is defined as the product of the index of reflection and the geometrical distance between the reflecting surfaces. Between the bright fringes, destructive interference occurs when the paths of the two rays differ by an odd number of half wave lengths and a dark fringe is observed. Since the distance between the surfaces is constant along any line, e.g., EE', perpendicular to the principal axis, i.e., ON as shown in Figure 1 (b), the fringes are spaced at a distance $d = \lambda/2n\theta$, provided the wedge angle is small. For a given wave length, λ, and wedge angle θ, the spacing is determined by the index of refraction, n. When two diffusing liquids are placed in contact in the wedge, a refractive index gradient is produced in the wedge and the fringes are displaced along the wedge in the region of changing refractive index so that they maintain a constant optical distance. In other words, each fringe represents a contour line of constant optical path in the wedge.

The interference pattern has two important characteristics on which the experimental method depends:

1. Along any line drawn parallel to the original interface, the distance between adjacent fringes is constant.

2. Along any line drawn perpendicular to the original interface, the change in refractive index between any two adjacent fringes is constant. If a straight line is drawn parallel to the straight fringes in the portion of constant refractive index, the reference line represents a line of constant thickness of the wedge. Therefore, the change of optical path along this reference line depends only upon change of the refractive index along this line. Consequently, if the fringe number is

plotted against the position of the intersection of the fringe and the reference line, the curve shows the relationship between the refractive index (and hence, the concentration) and distance along the reference line. Similarly, if the density of fringes along the reference line is plotted against position, the refractive index gradient (and, hence, the concentration gradient) versus distance is obtained. Therefore, if the direction of the diffusion is parallel to the straight fringes, the diffusion coefficient may be calculated.

EXPERIMENTAL APPARATUS

The experimental apparatus used in this investigation were diffusion apparatus, viscometer and refractometer.

(A) Diffusion apparatus

A diagrammatic sketch of the diffusion apparatus is shown in Figure 2. L is a gas laser. The narrow cone of coherent monochromatic light from the laser is directed on to the flat microscope mirror, R. This front surface mirror reflects the light beam upward through the diffusion cell, W, which rests on a temperature controlled microscope stage, H. The lenses of the microscope focus the interference image through the camera shutter, S, onto the photographic film at F. The camera back is provided with a mirror which may be swung into a position in front of the film so that the image appears on the ground glass viewing screen, G. The detail description of each part of the apparatus are as following:

(1) Light source

A model 5200 gas laser of the Perkin-Elmer Corp. was used as the source of polarized, coherent, monochromatic radiation. This radiation

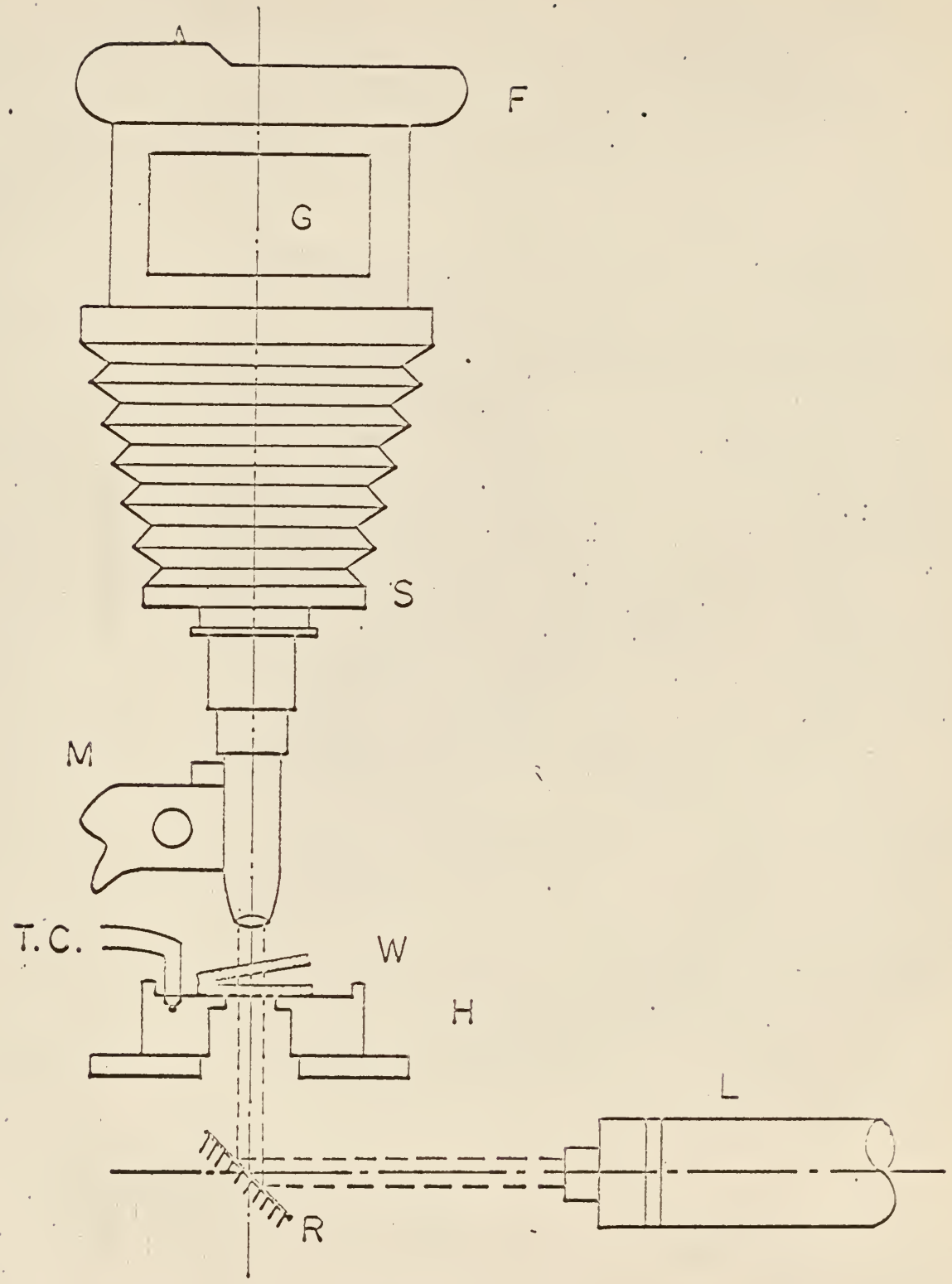


Fig.2. The diagram of the diffusion apparatus.

was excited at 6328 Å, by means of a model 5202 dc power supply. Both are shown in Figure 3.

(2) Cell

The diffusion cell consists of two partially metallized plate glass microscope slides separated by a spacer at one end to form the wedge. The slides were metallized on one side so that they were partly transmitting and partly reflecting to light. Increasing the reflectivity of the plates will increase the sharpness of the fringes, but also decreases the intensity of the image to be photographed. Nishijima and Oster (30) have recommended a reflectivity of 80 to 90%.

(3) Microscope

An ordinary Bausch & Lomb student series microscope body and stage were used without the slide-in condenser lens. However, the objective and ocular were especially selected for this photographic work. The objective selected was a Bausch & Lomb Achromatic which had a 30 mm focal length, N. A. 0.09, and a magnification of 3.5x. The ocular was a Bausch & Lomb ultraplane lens with magnification of 7x.

(4) Camera

The microscope was mounted on the Bausch & Lomb Model L basic photomicrographic equipment as is shown in Figure 4. The camera, which was mounted on the upright, was supplied with a number 4 exposure shutter. The shutter was coupled to the microscope by a light-tight connector. For this work the refractive back with a Polaroid Land attachment was found to be very satisfactory.

(5) Stage

Figure 5 is a close view of the diffusion cell assembled in position on the microstage. This stage was especially designed for temperature

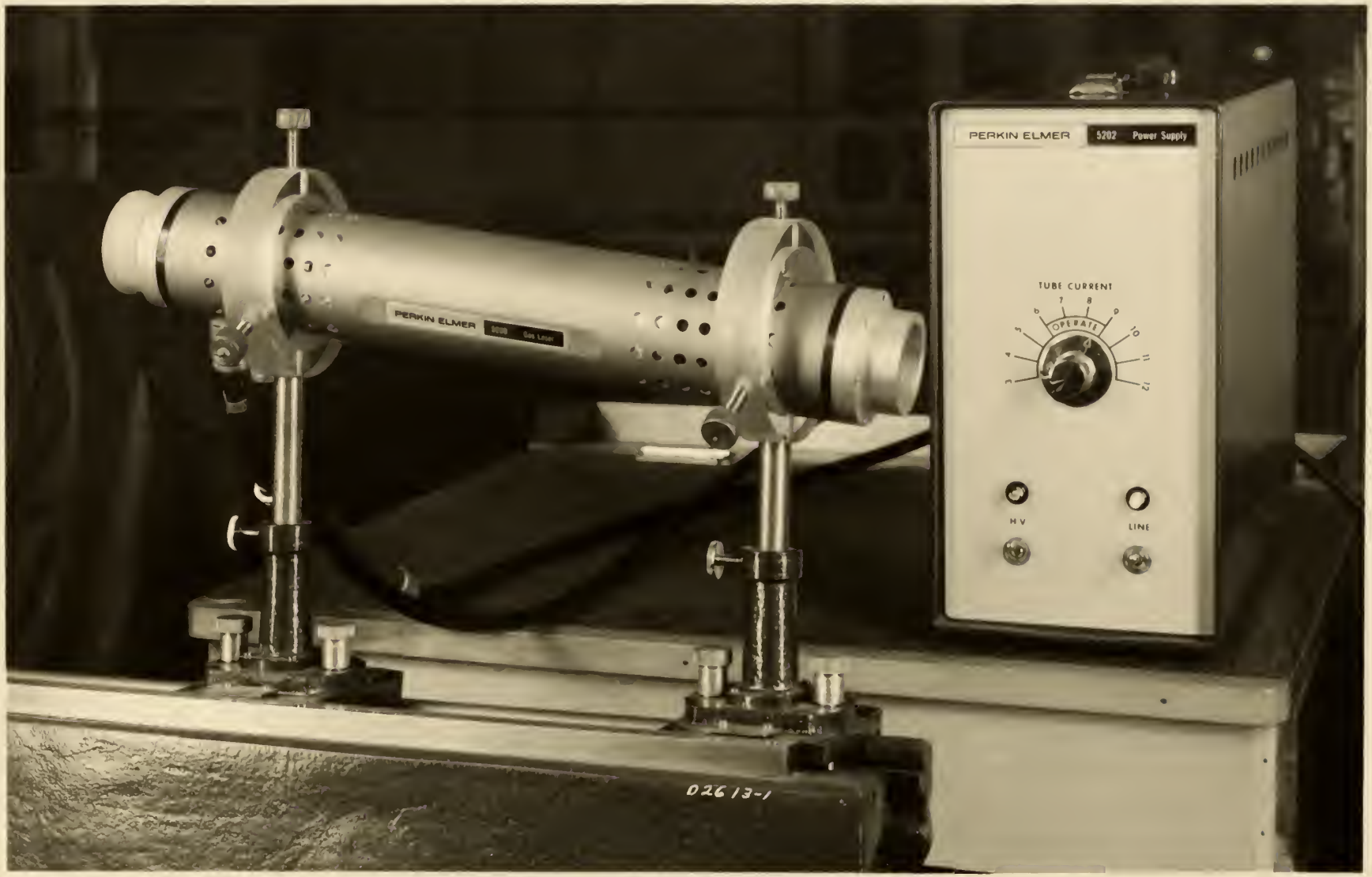


Fig. 3. The laser light source mounted on the optical bench .

Fig. 4. The Bausch & Lomb camera and other apparatus for the measurement of the diffusivity of a liquid .

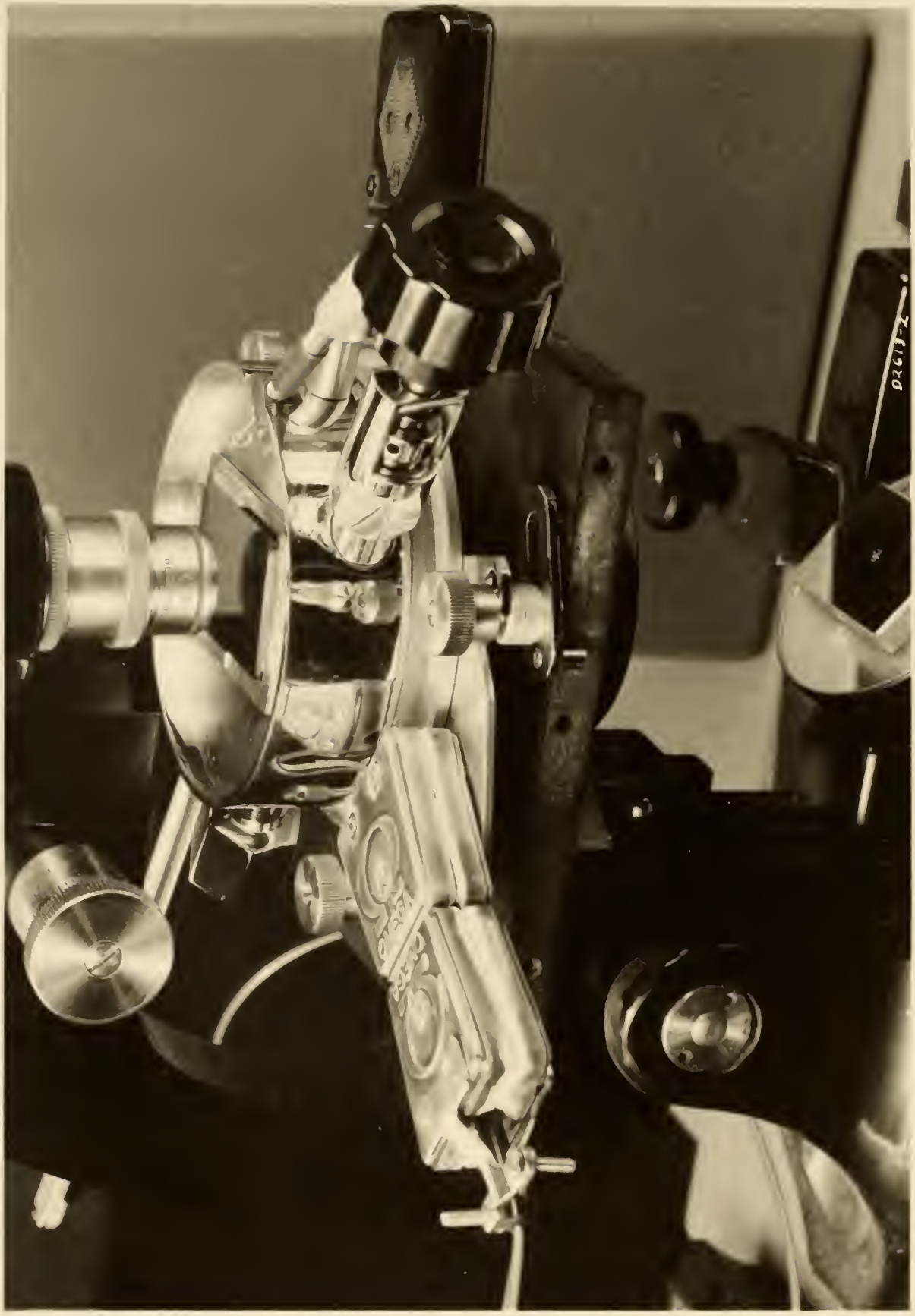


Fig. 5.4 The diffusion cell on the micro-stage.

control of microscope slides by Kofler. This stage could be either heated electrically to obtain a temperature higher than ambient temperature or cooled by carbon dioxide expansion as desired.

The Kofler stage was modified by the addition of a copper-constant an thermocouple. Figure 5 also shows the jig which was designed to facilitate the assembly and manipulation of the diffusion cell at the start of each experiment. The jig consisted of brass frame which surrounds the wedge. Four guide blocks were soldered to the upper surface of the frame, one block on each side. This design did not interfere with the assembly of the wedge and provided a means of manipulating the assembled wedge on the stage.

(B) Coordinate measuring apparatus

Figure 6 shows the Leitz-Wetzlar 6x6 inch coordinate measuring microscope. This was used to measure the positions of the fringe intersections with the reference line. Beneath the microscope tube is the light box mounted upon the micrometer table. This table can be moved along two horizontal axes at right angles to each other and also rotated in the same horizontal plane.

(C) Viscosity measuring apparatus

The Cannon-Fenske routine type viscometer is shown immersed in the water bath in Figure 7. The viscometer used in this work was manufactured by Fisher Scientific Co. to ASTM specifications. A constant temperature environment for the viscosity measurements was provided by a thermostatic water bath manufactured by E. H. Sargent & Co..

(D) Refractivity measuring apparatus

The refractometer used in this study was the Bausch & Lomb type Abbe-3L refractometer. The temperature controller was a Haake, Berlin

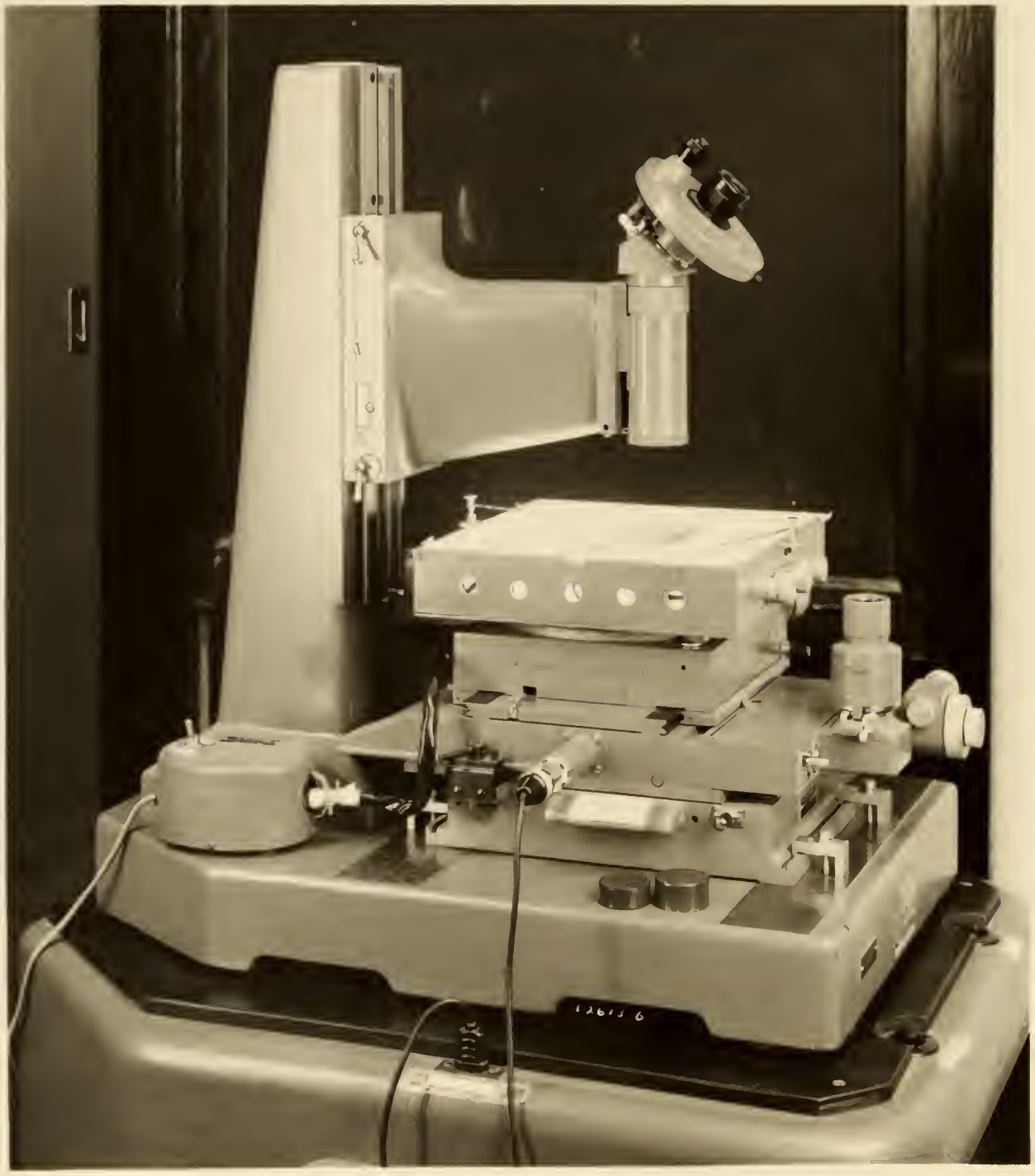


Fig. 6. The coordinate measuring microscope with a photographic plate in position on the top of the light box.

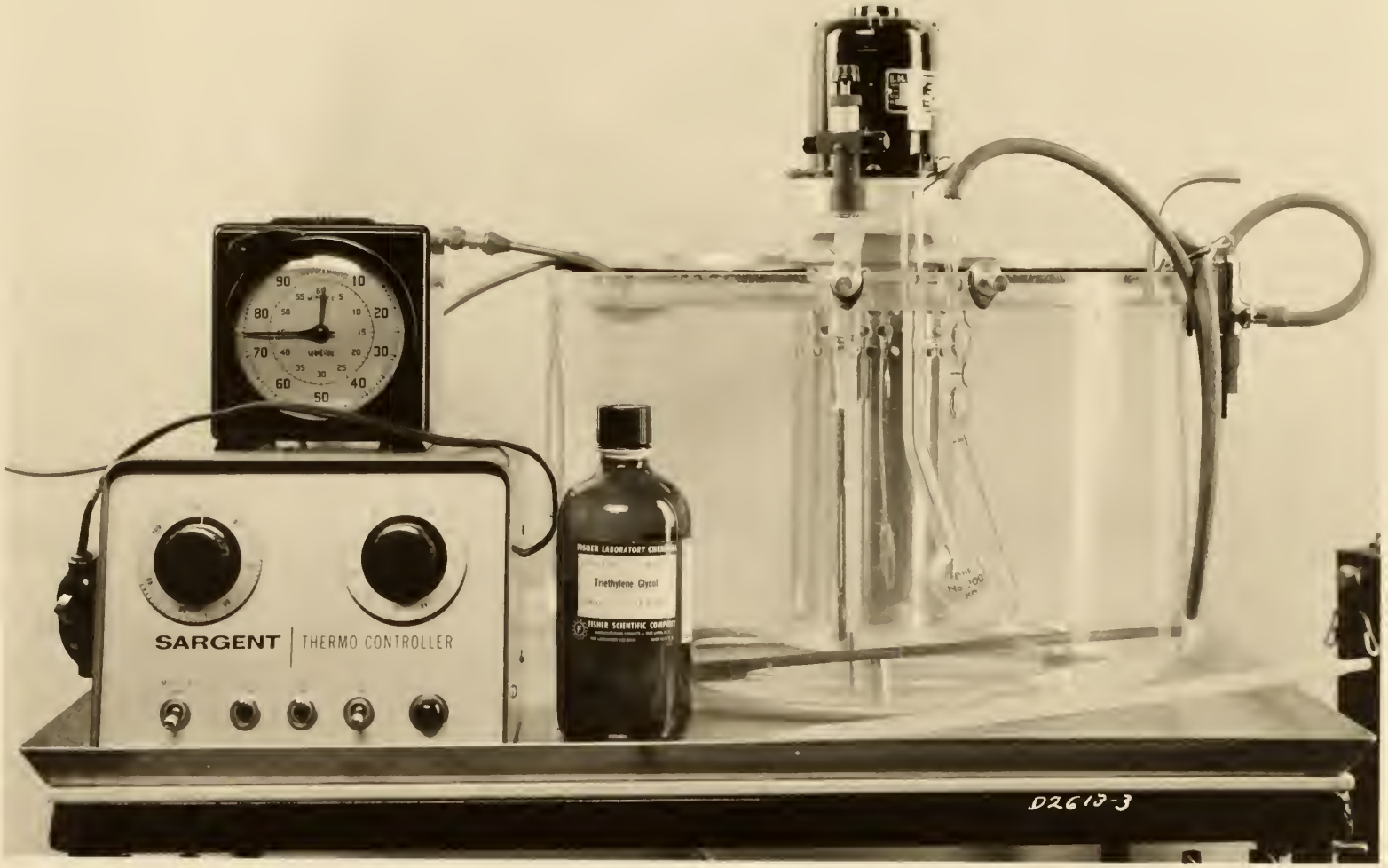


Figure 7. The apparatus assembled for the measurement of the viscosity of a liquid.

Circulator Series "ED". The unit was mounted on the edge of an open water bath.

EXPERIMENTAL PROCEDURE

The procedure for making a diffusion run was as follows: One of the slides was set on the microscope stage with the metallized surface facing upward. One drop of each of the two liquids at different concentration was placed on the slide near each other. The spacer was placed at one end of the slide and the second metallized slide was slowly placed over it with its metallized surface down to make a wedge, forcing the two drops to merge. Immediately after the formation of the interface, the stopwatch was started. A range was chosen in the microscope where the sharp boundary was at right angles with the fringes, and photographs were taken at regular intervals.

EVALUATION OF DIFFUSIVITY

The data from the diffusion experiment consisted of the positions along the reference line where each fringe intersected it on a series of photographic plates and the time from the start of the run until the photographic plate was made. The diffusivity was calculated from these data as follows:

The first step was to determine the gradient of the refractivity along the reference line. A numerical method was employed for this calculation.

The second step was to fit a mathematical model to these observed refractive index gradients. From these two steps, the diffusivity was calculated. Digital computer programs for the IBM-1620 and the IBM-1410 computers were employed in this work. Detailed information about the

determination of the gradient of refractivity and the model fitting as well as the computer programs and their operation are available in Jerom's thesis (2).

CHAPTER IV

DIFFUSIVITY OF HONEY-WATER SYSTEM AT 25 °C

MATERIALS

Honey is the natural food of the honey bee, gathered by them as nectar from the nectaries of plants, modified and stored in their combs. Honey is laevorotatory, containing not more than twenty five per cent of water, not more than twenty five hundredths per cent of ash, and not more than eight per cent sucrose.

According to Brown and Young (31) the average composition of honey is

H_2O	17.6 %
fructose	40.5 %
glucose	34.0 %
sucrose	1.9 %
others	6.0 %

The honey used in this investigation was "3 Bears Honey" marketed by R. D. Bradshaw & Sons, Wendell, Idaho. Honey was dissolved in distilled water to prepare samples with different concentrations. The water content of the original sample was within approximately 1% of that quoted above.

VISCOSITY

The viscosities of the honey solutions were obtained with a Cannon-Fenske routine type viscometer and densities were measured with a 25 cc glass specific gravity bottle. The results of this work are recorded in Table 1 and plotted in Figure 8 where the viscosities are shown as a function of mass fraction.

Table 1.

Viscosities and Densities of Aqueous Honey Solutions at 25 °C

Concentration wt. % honey	Density grams/cc	Viscosity poises
94.47	1.4325	18.255
89.71	1.375	2.883
79.636	1.281	0.894
64.794	1.218	0.163

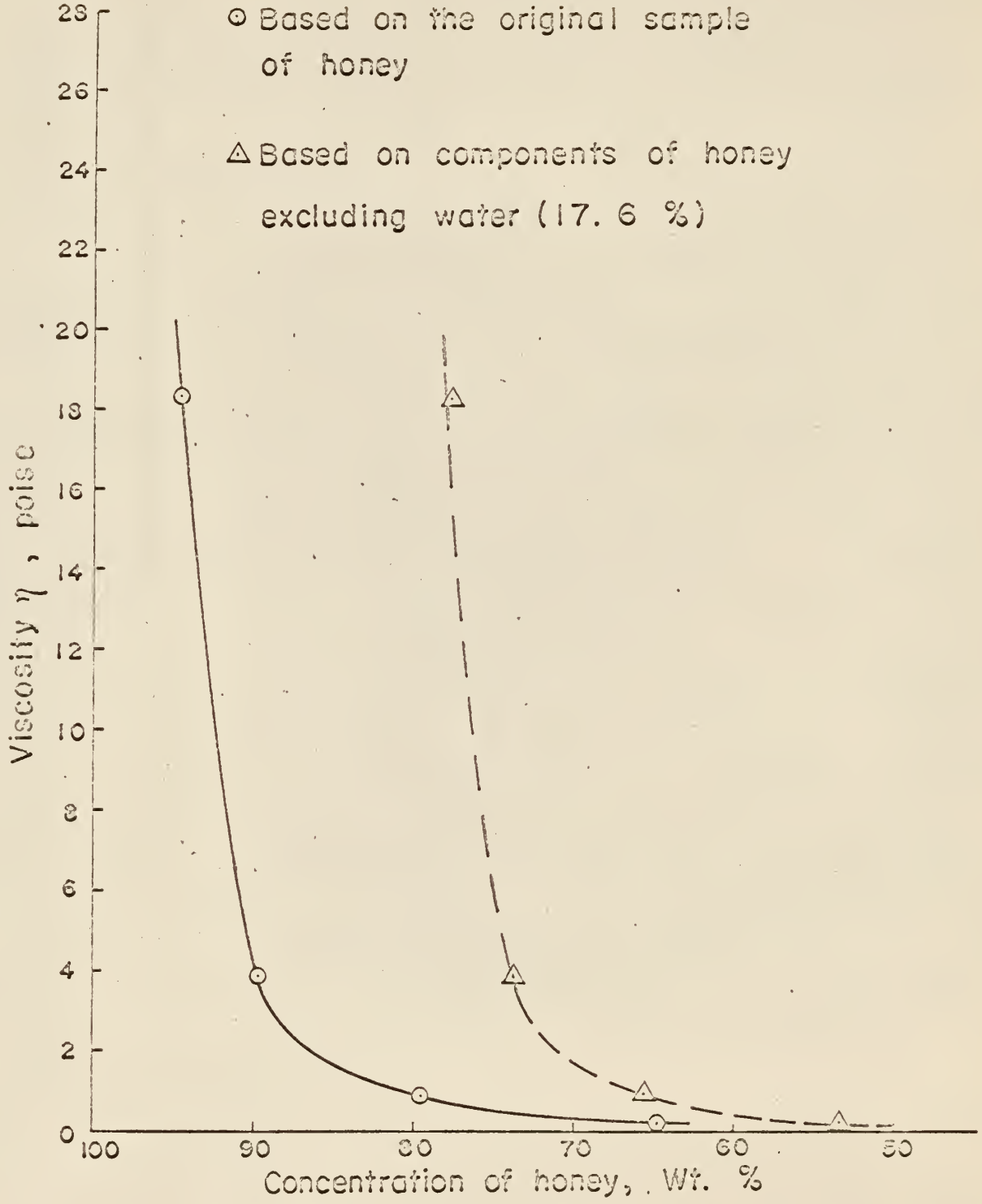


Fig. 8. Viscosity vs. concentration for honey-water system at 25 °C.

From Figure 8 one can see that the viscosity changes rapidly at higher concentration range (concentration of honey higher than 90 wt. %). As will be seen later, the diffusivity also undergoes a fairly drastic change in the vicinity of this concentration.

REFRACTIVE INDEX

The refractive index was determined with the Bausch & Lomb type Abbe-3L refractometer. The results are summarized in Table 2 and also plotted in Figure 9. It can be seen that the refractive index is closely linear with concentration in the range of interest. This satisfies the assumption required to derive equation II-6.

DIFFUSIVITY

The experimental diffusivities were obtained by measuring the inter-diffusion of two solutions of slightly different concentrations using a micro-interferometric method as described previously. Four pairs of solutions were measured at atmospheric pressure and at 25±0.3°C. These pairs of solutions are

{ pure (commercial) honey
{ 93.51 wt. % honey solution

{ pure (commercial) honey
{ 85.94 wt. % honey solution

{ 85.94 wt. % honey solution
{ 74.92 wt. % honey solution

{ 74.92 wt. % honey solution
{ 65.41 wt. % honey solution

Strictly speaking, however, equation II-5 is valid only for binary diffusion. For a multicomponent system, the corresponding equation is

Table 2.

Refractive Indices of Aqueous Honey Solutions at 25 °C

Concentration wt. % honey	Refractive Index
93.51	1.4819
85.94	1.4699
65.41	1.4453

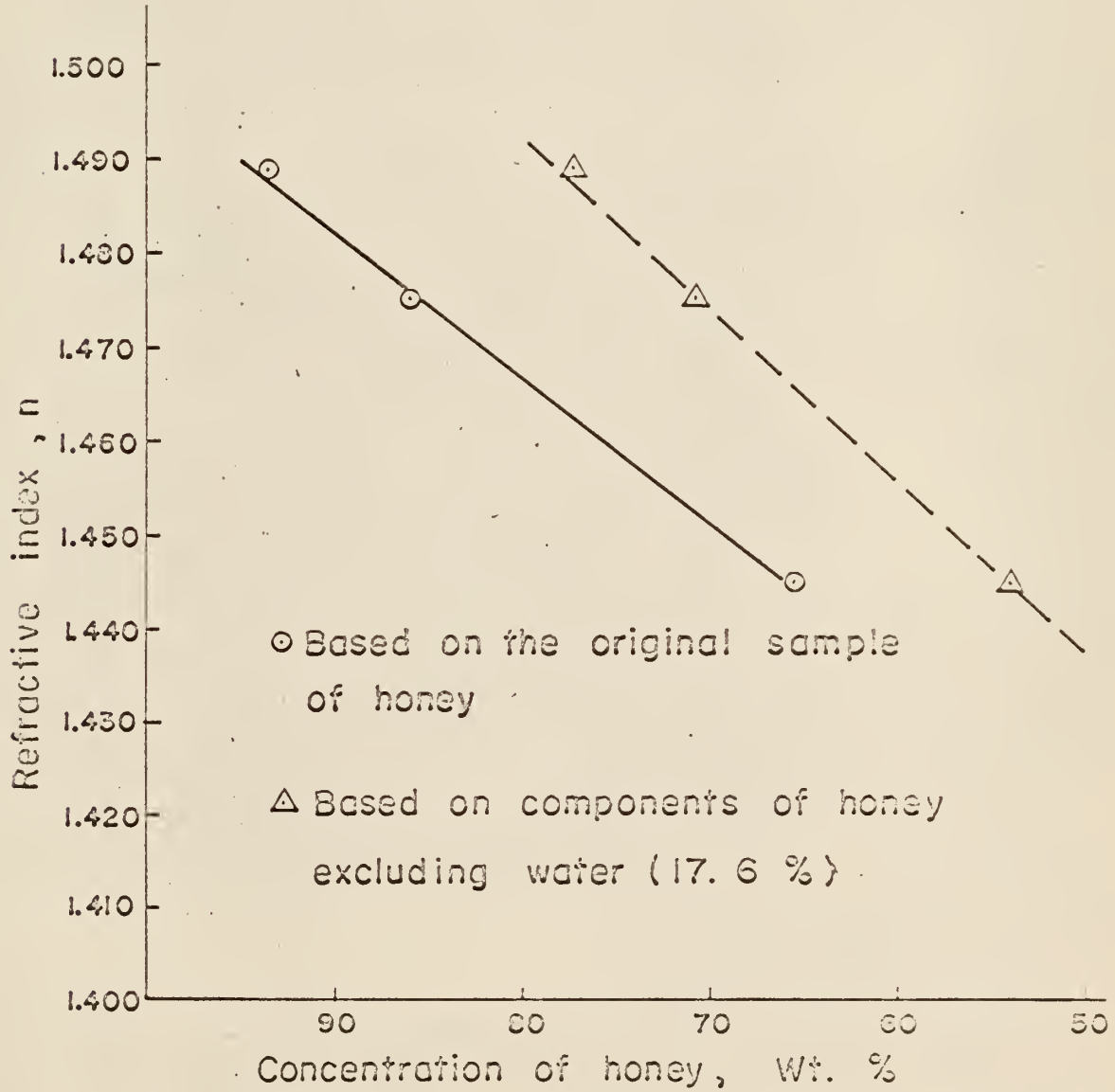


Fig. 9. Refractive index vs. concentration for honey – water system at 25 °C.

is more complicated (5). In this study we consider honey as the first component and water as the second component and use equation 5 to calculate the so-called "apparent binary diffusivity".

Values of the experimental diffusion coefficients, D_{AB}, and the respective initial and mean concentrations, Co', Co", $\bar{C}$, of the solutions are given in Table 3 and are also plotted in Figure 10. From Figure 10 one sees that the diffusivity can be correlated approximately by two lines represented by

$$D_{AB} \times 10^6 = 10.72 - 11.35C, \text{ for } C \leq 0.93 \text{ wt. fraction}$$

$$D_{AB} \times 10^6 = 6.677 - 5.57\ C, \text{ for } C \geq 0.93 \text{ wt. fraction} .$$

The concentration, C, in these expressions is based on the weight of the original honey sample. A fairly drastic change in the diffusivity occurs at the concentration in the vicinity of 93 wt. %. A drastic change of viscosity, η, also occurs at approximately the same concentration as shown in Figure 8. Above 90 wt. % of honey concentration, water probably serves as solute but below that, it behaves as solvent. The apparent diffusivities as shown in Figure 10 are strongly dependent on concentration. There is almost a 30 fold difference between the highest and lowest measured values. It is, therefore, not correct to assume D_{AB} as a constant in a wide range of concentration.

In Figure 10 the measured apparent diffusivities are also plotted against the concentration excluding water. The major composition of honey is glucose. Other components, except water, are structurally similar to glucose. Therefore, one can predict that the apparent diffusivity of honey has the same order of magnitude as glucose.

Table 3.

Diffusivity of Honey-Water System at 25 °C

Initial concentration, wt. fraction of honey			Diffusivity
C'	C''	$\overline{C}$	$D_{AB} \times 10^6$ cm^2/sec
0.6541	0.7492	0.7016	2.76
0.7492	0.8594	0.8043	1.62
0.8594	1.0	0.9297	0.149
0.9351	1.0	0.9675	0.130

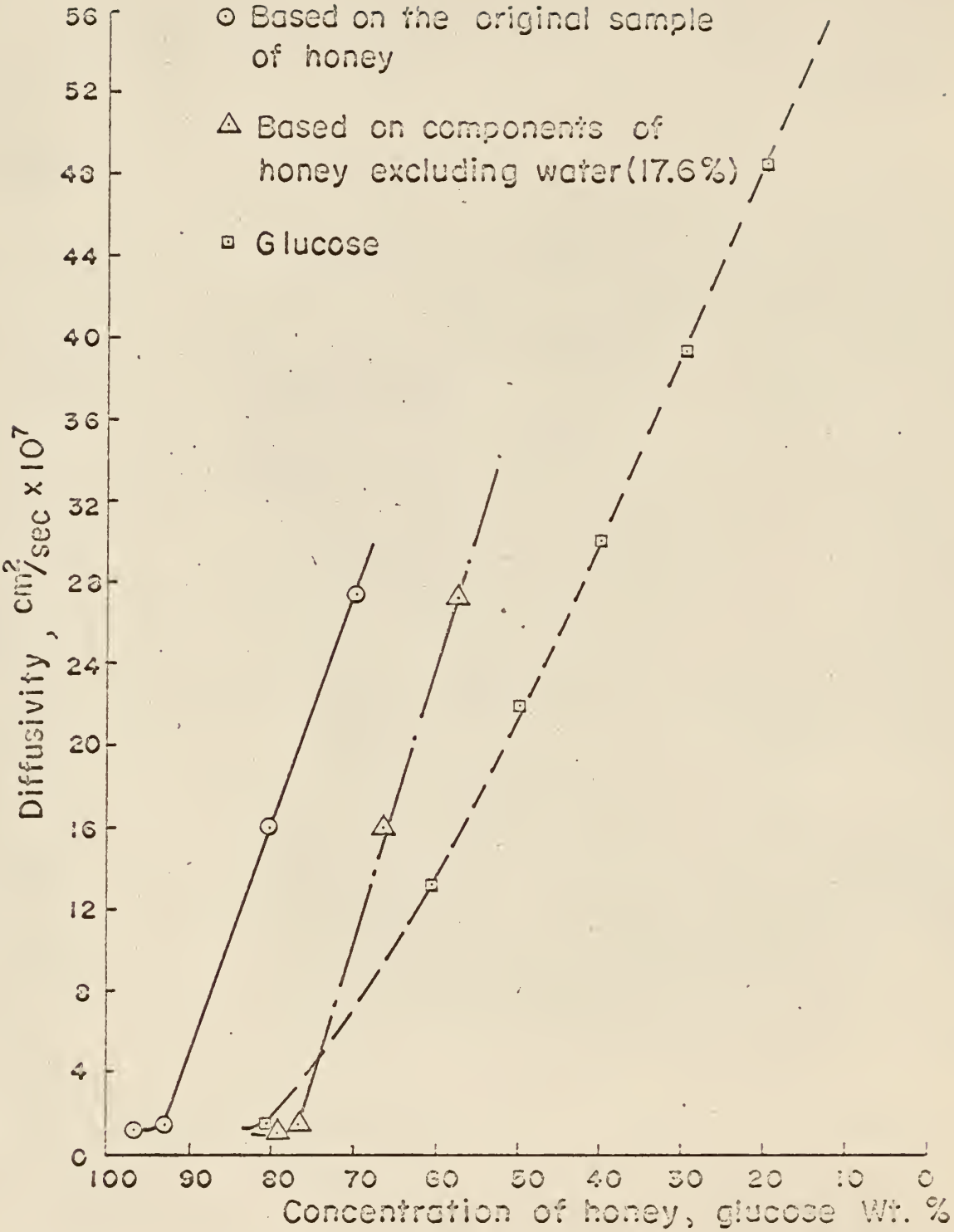


Fig. 10. Diffusivity vs. concentration for honey–water and glucose–water systems.

The diffusivities of glucose in water (32) are plotted in Figure 10 for comparison.

The Stokes-Einstein equation for a pure system can be written as (5)

$$D_{AB}\eta = \frac{KT}{6\pi r} \qquad (1)$$

where K is Boltzmann's constant, T is absolute temperature, and r is the radius of the diffusion particle. In this work values of D_{AB} were calculated by using the viscosity of the solution instead of the solvent. The results are presented in Table 4 and also plotted in Figure 11. One sees that the change of $D_{AB}\eta$ is less pronounced than the change of individual transport properties as predicted by this equation.

Table 4.

$D_{AB}\eta$ of Honey in Different Concentrations

Concentration wt. % honey	Viscosity poises	Diffusivity $D_{AB} \times 10^6$ cm^2/sec	D_{AB} dynes
70.16	0.26	2.76	0.717
80.43	8.95	1.62	1.539
92.97	11.0	0.149	1.639
96.75	27.0	0.130	3.510

CHAPTER V

DIFFUSIVITIES OF DIETHYLENE GLYCOL-WATER SYSTEM AT 25°C

MATERIALS

Diethylene glycol is an aliphatic organic compound having two hydroxyl groups per molecule. It resembles water in that it is an essentially clear, colorless liquid with practically no odor. The molecular formula is $C_4H_{10}O_3$ and the molecular weight is 106.1.

The diethylene glycol for this investigation was purchased from Matheson, Coleman and Bell Co. The material was graded as superior by the manufacturer and was used without further purification. Some physical properties of pure diethylene glycol are listed in Table 5 for reference. The solutions were prepared with double-distilled water.

Since diethylene glycol is extremely hygroscopic, the prepared solutions were sealed in bottles to eliminate absorption of moisture from the air.

VISCOSITY

Pure diethylene glycol is about 30 times as viscous as water and its viscosity varies inversely with temperature, as does that of most substances. The viscosity-composition relationship of the diethylene glycol-water system is very non-linear. The values listed in Table 6 and shown in Figure 12 were obtained from a publication "Glycols, Properties and Uses," by Dow Chemical Company.

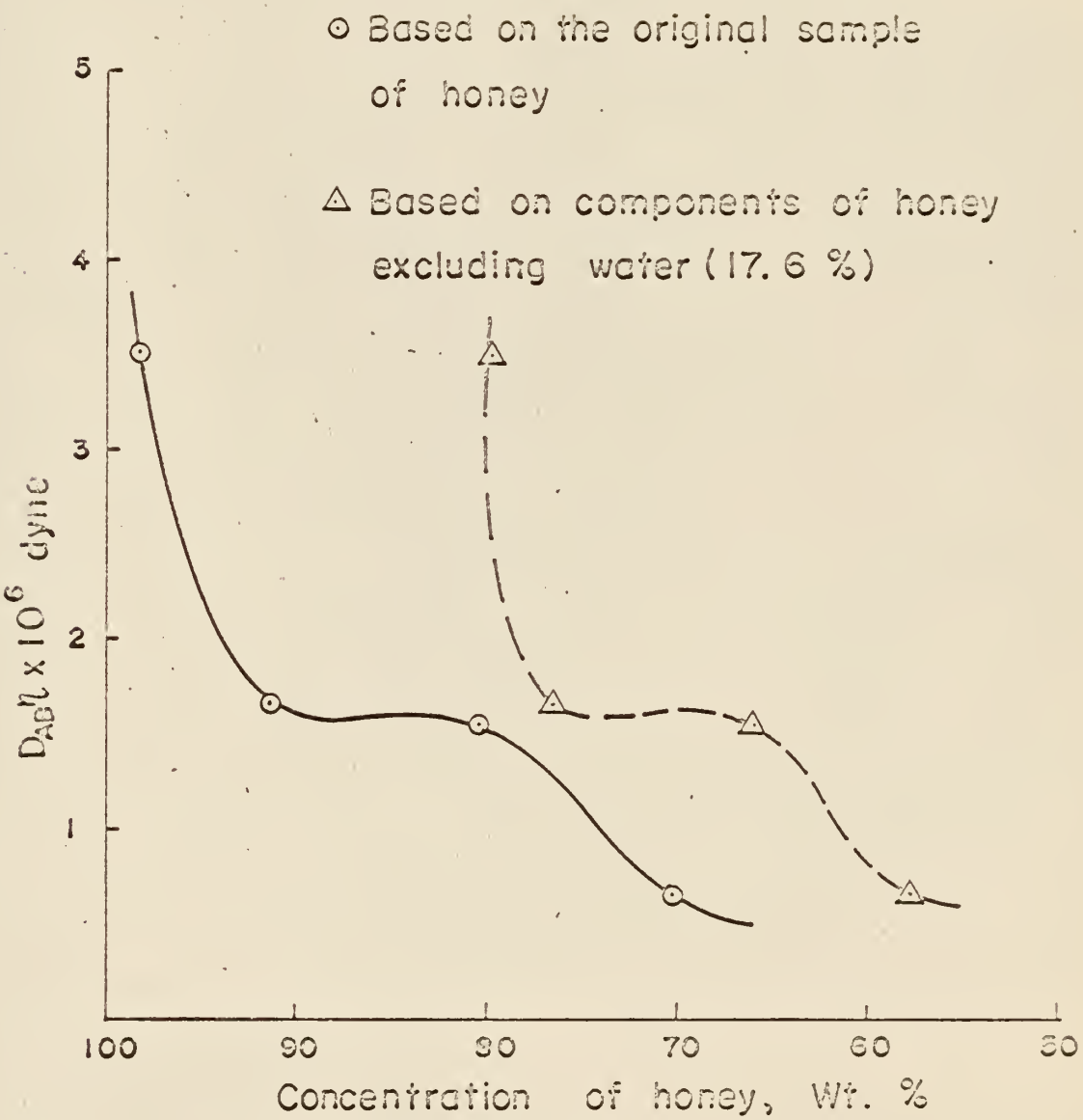


Fig.11. The $D_{AB}\eta$ vs. concentration for honey-water system.

Table 5.

Physical Properties of Diethylene Glycol*

Boiling point at 760 mm Hg	472.6°F. (244.8°C)
Vapor pressure at 77°F (25°C)	0.01 mm Hg.
Density at 77°F (25°C)	1.113 g/cm^3
Freezing point	17°F (-8.33°C)
Surface tension at 77°F (25°C)	44 Dynes/cm
Specific heat at 77°F (25°C)	0.55, BTU/lb °F
Flash point	280°F (137.7°C)

*Glycol properties and uses; the Dow Chemical Company (1956)

Table 6.

Viscosities of Diethylene Glycol Solutions at 25°C

Concentration wt. % Glycol	Viscosity Centipoises
100	28.2
90	20.5
80	14.5
70	9.5
60	6.9
50	4.4
40	3.0
30	2.1
20	1.5
10	1.2
0	0.8937

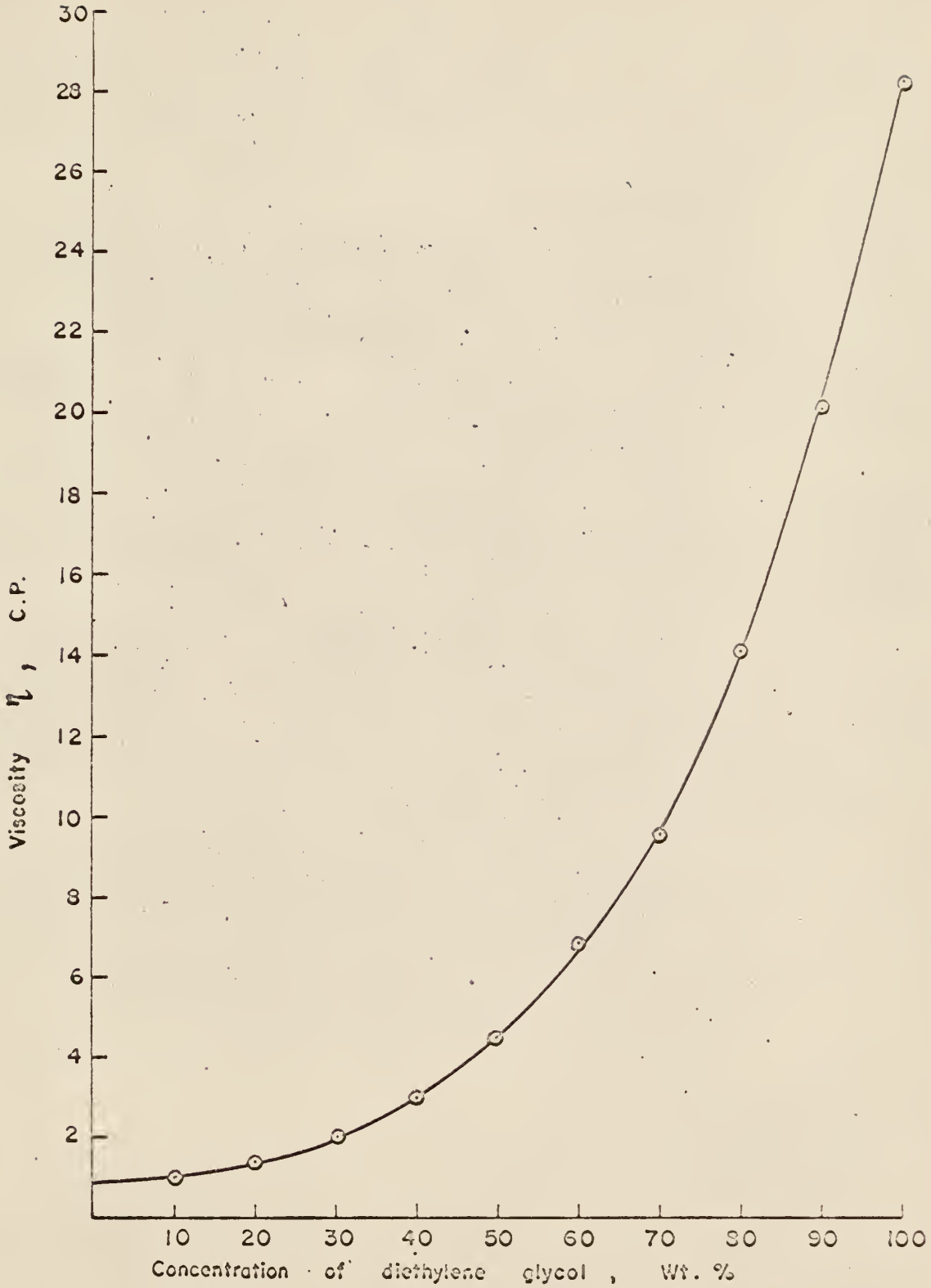


Figure 12. Viscosity vs. concentration for diethylene glycol - water system at 25°C

REFRACTIVE INDEX

The refractive indices of pure and aqueous diethylene glycol solutions measured with the Bausch & Lomb type Abbe-3L refractometer are summarized in Table 7 and also plotted in Figure 13. Although the refractive index of aqueous diethylene glycol solution is not a linear function of composition, it can be assumed to be so for small concentration ranges. This is a necessary assumption for deriving equation II-6, repeated below.

$$\frac{\partial n}{\partial z} = \frac{n_o'' - n_o'}{2\sqrt{\pi D_{AB} t}} \exp\left(-\frac{z^2}{4D_{AB}T}\right) . \qquad \text{(II-6)}$$

DIFFUSIVITY

The experimental diffusivities were obtained by measuring the interdiffusion of two solutions of slightly different concentrations using a microinterferometric method as described previously. Seven pairs of solutions were measured at atmospheric pressure and at 25±0.3°C. These pairs of solutions were:

{ pure diethylene glycol
  86.47 wt. % (0.52 mole fraction) diethylene glycol solution

{ 86.47 wt. % (0.52 mole fraction) diethylene glycol solution
  72.23 wt. % (0.306 mole fraction) diethylene glycol solution

{ 72.23 wt. % (0.306 mole fraction) diethylene glycol solution
  56.85 wt. % (0.184 mole fraction) diethylene glycol solution

Table 7.

Refractive Index of Diethylene Glycol and its Aqueous Solutions at 25°C

Concentration wt. % Glycol	Refractive Index
100	1.4450
86.47	1.4325
72.23	1.4175
55.62	1.3983
41.80	1.3820
25.07	1.3620
0.00	1.3324

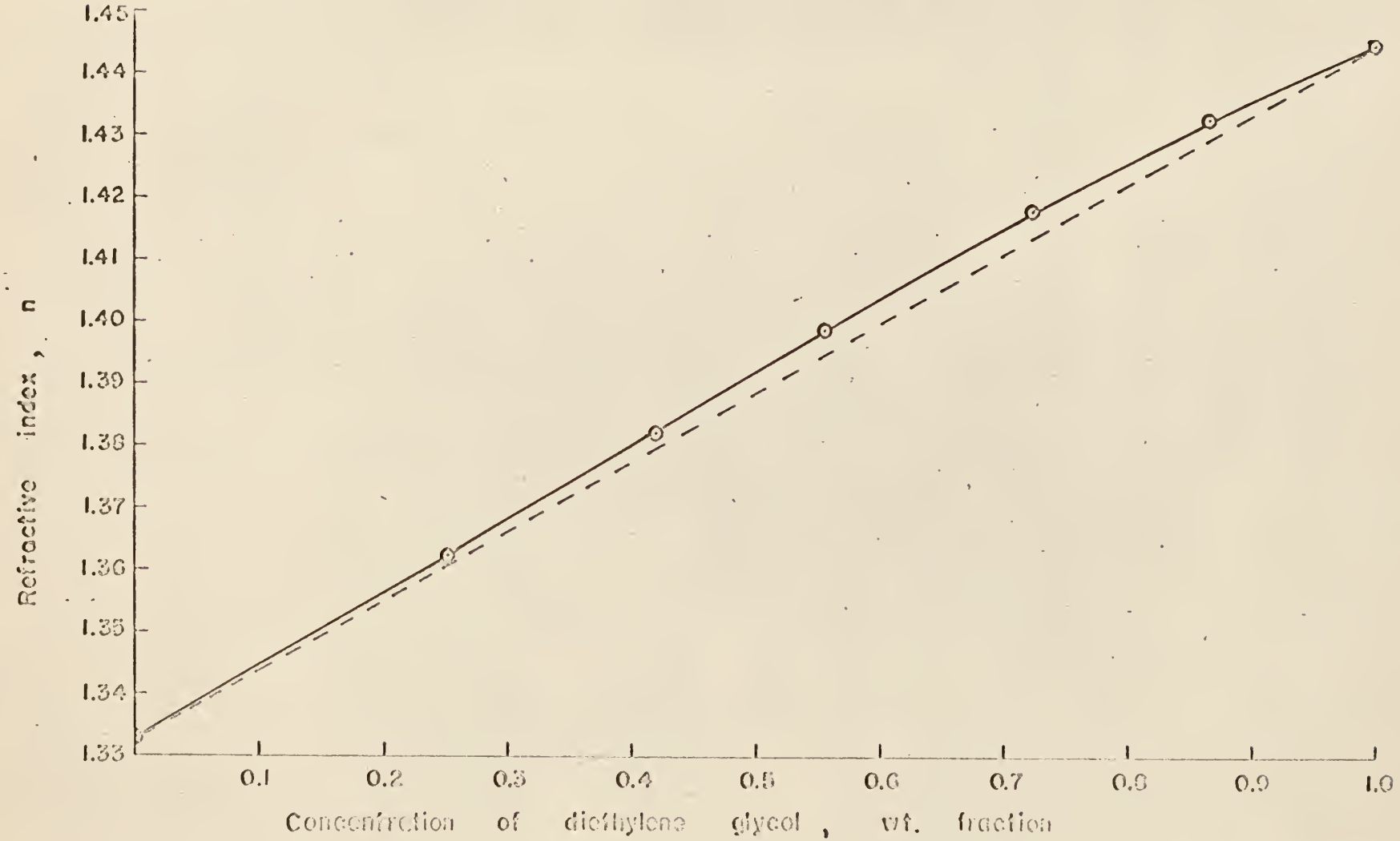


Figure 13. Refractive indices vs concentration for diethylene glycol - water system at 25° C

{ 56.85 wt. % (0.184 mole fraction) diethylene glycol solution
  43.08 wt. % (0.114 mole fraction) diethylene glycol solution

{ 43.08 wt. % (0.114 mole fraction) diethylene glycol solution
  26.96 wt. % (0.059 mole fraction) diethylene glycol solution

{ 26.96 wt. % (0.059 mole fraction) diethylene glycol solution
  11.25 wt. % (0.021 mole fraction) diethylene glycol solution

{ 11.25 wt. % (0.021 mole fraction) diethylene glycol solution
  pure water

Values of the experimental diffusion coefficients, D_{AB}, and the respective initial and mean concentrations, Co', Co", $\overline{C}$, of the solutions are given in Table 8. Figures 14 and 15 show the concentration dependence of diffusivities. Tables AII-1 through AII-6 in Appendix II give the complete record of the experimental results of this investigation.

Figure 14 shows the diffusivity as a function of weight fraction of diethylene glycol while the diffusivity is plotted as a function of mole fraction in Figure 15. From these two figures one can see that the diffusivity decreases with increasing glycol concentration. Since viscosity is a measure of internal resistance to the flow of a fluid, the diffusivity should vary inversely with viscosity. This is roughly the case.

For a non-associated solution, ideal or non-ideal, liquid or solid, log (D_{AB}) usually varies linearly with mole fraction (33). In the case of associated solutions, the exponential variation is found whenever the average degree of molecular association of the associated

Table 8.

Summary of Experimental Diffusivities for Diethylene Glycol-Water System at 25°C

C_0' (glycol)		C_0'' (glycol)		$\bar{C}$ (glycol)		Diffusivity, $D_{AB} \times 10^6$
wt. %	mole %	wt. %	mole %	wt. %	mole %	cm^2/sec
100	100	86.47	52.02	93.23	76.01	1.68
86.47	52.02	72.23	30.61	79.35	41.31	2.41
72.23	30.61	56.85	18.36	64.54	24.48	4.63
56.85	18.36	43.08	11.37	49,96	14.86	7.54
43.08	11.37	26.96	5.89	35.02	8.63	13.2
26.96	5.89	11.25	3.85	19.10	4.87	19.1
11.25	3.85	0.00	0.00	5.62	1.92	25.0

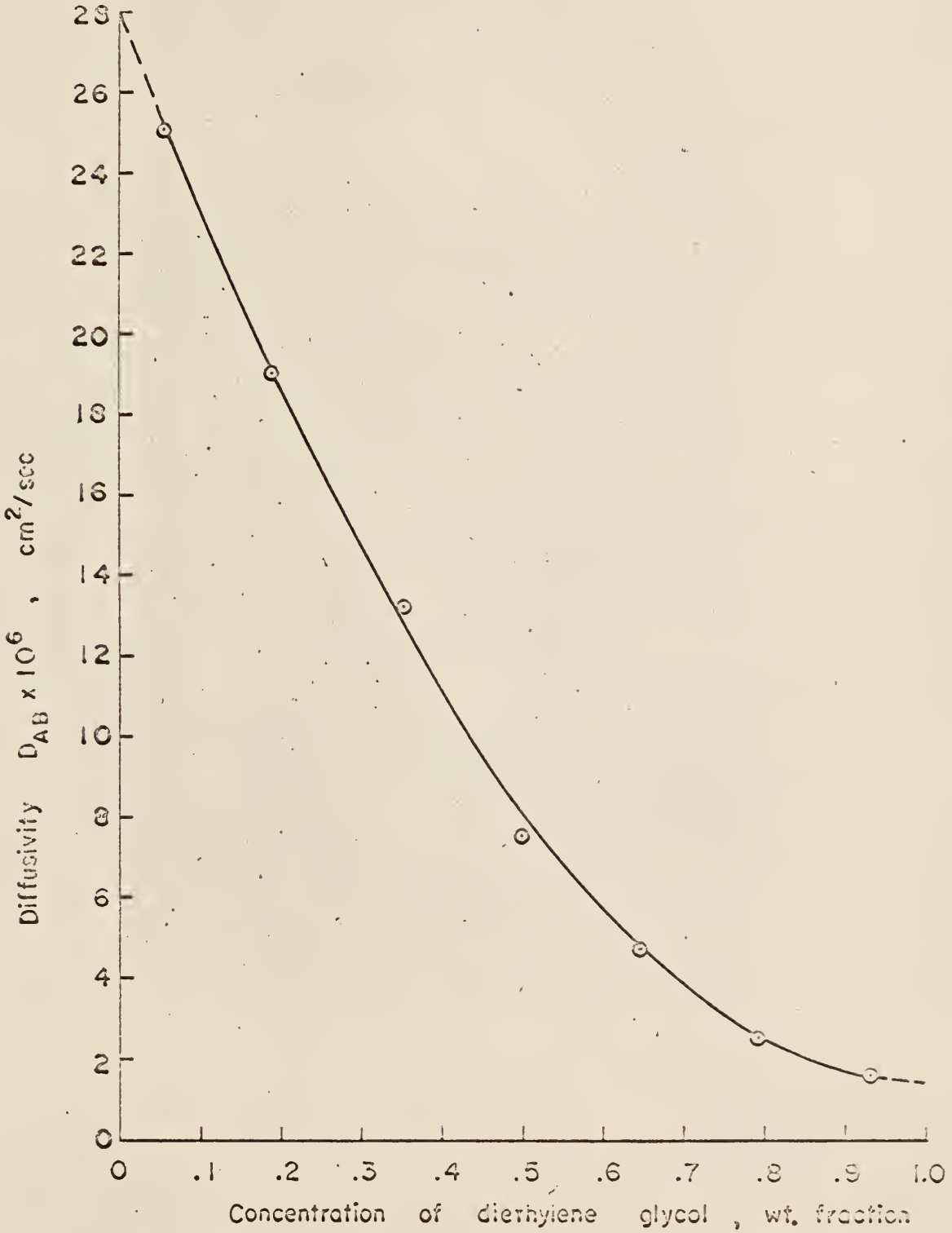


Figure 14. Diffusivity vs concentration for diethylene glycol - water system at 25° C.

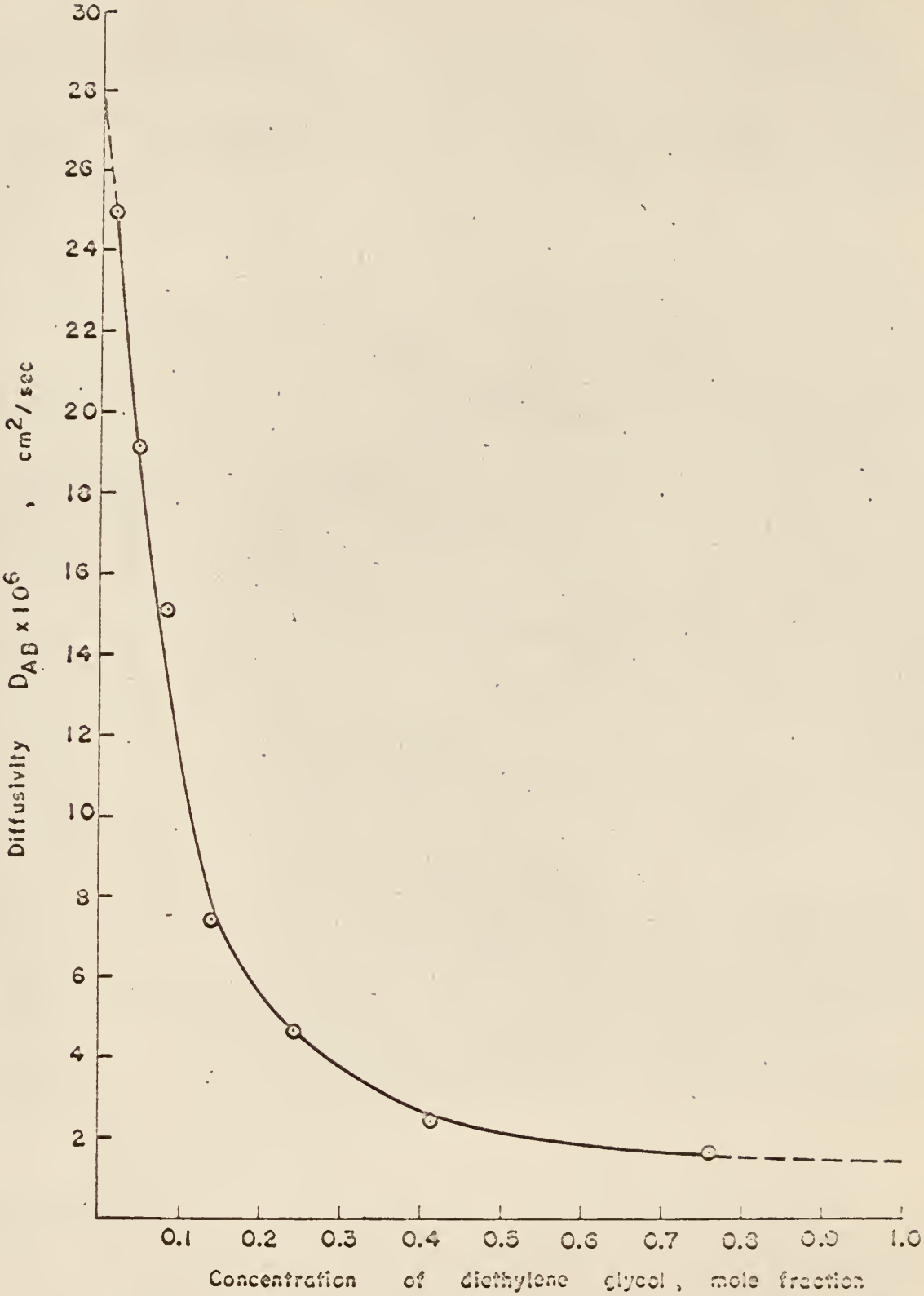


Figure 15. Diffusivities vs concentration for diethylene glycol - water system at 25° C

compound can be considered constant. Log (D_{AB}) is plotted against concentration in Figure 16, and the two apparently straight line segments intersect near the concentration 0.3 mole fraction of diethylene glycol. This may be due to a large change in degree of association or of liquid structure in this concentration range.

ANALYSIS OF RESULTS

As mentioned previously, no satisfactory theories of the liquid state exist. Consequently no rigorous theories of diffusion for liquids have been proposed. The hydrodynamic theory which was discussed in chapter II leads to (8, 9)

$$D_{AB} = \frac{KT}{6 \pi \eta_o r_A} \qquad (1)$$

which is usually called the Stokes-Einstein equation. Equation 1 may be written in the form

$$D_{AB} \eta_o = \frac{KT}{6 \pi r_A} \qquad (2)$$

If the viscosity of solvent, η_o, is replaced by the viscosity of the solution, η, in equation 2, one can see that at constant temperature, $D_{AB} \eta$ should be a constant in the whole concentration range if the molecular radius, r_A of the solute can be assumed constant. A plot of $D_{AB} \eta$ vs concentration is shown in Figure 17. From this figure, one can see that $D_{AB} \eta$ values are roughly constant except in the range between 0.05 and 0.15 mole fraction glycol, where $D_{AB} \eta$ increases very rapidly. An extension of this theory gives rise to the definition of an

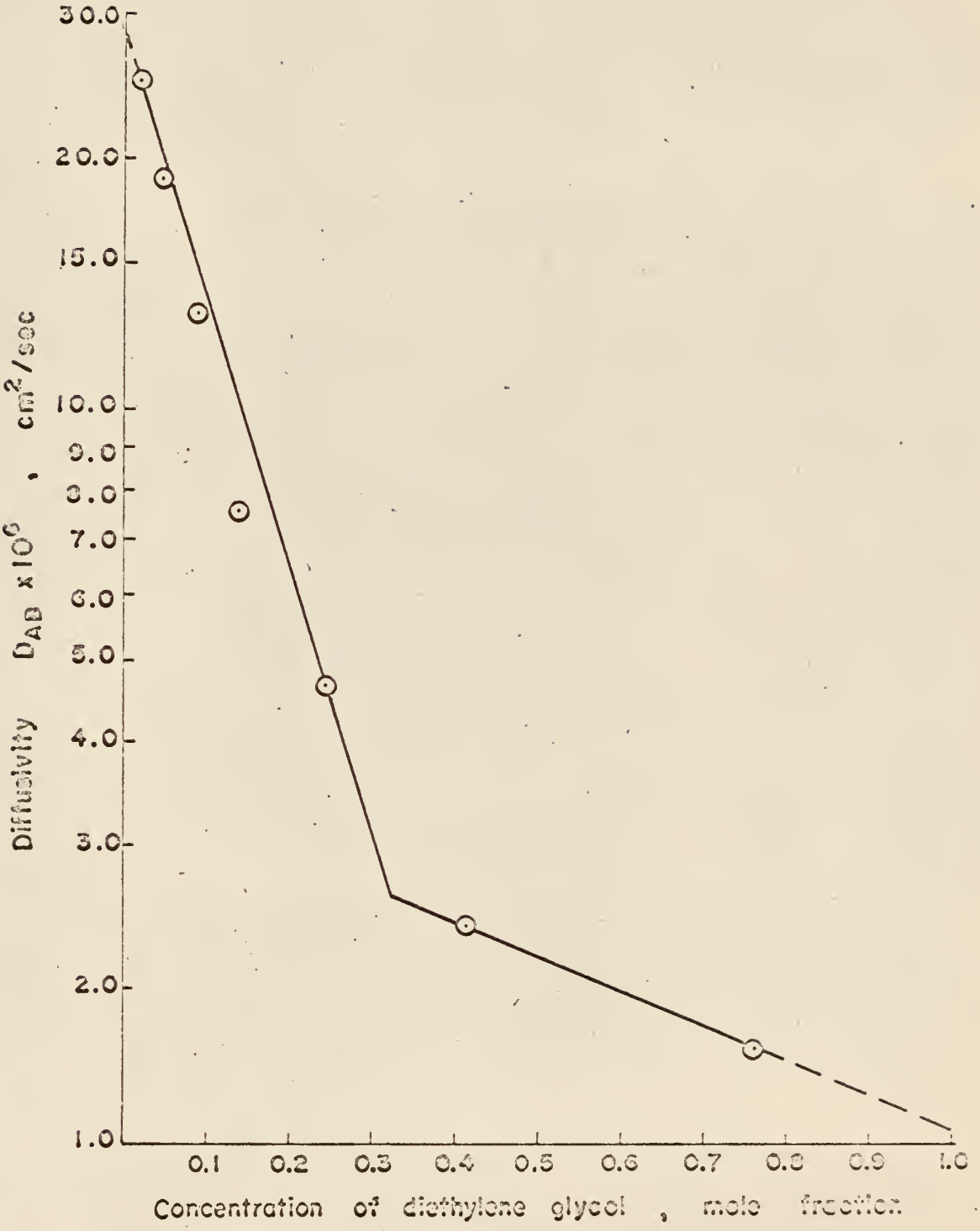


Figure 16. Diffusivity vs. concentration for diethylene glycol - water system at 25° C

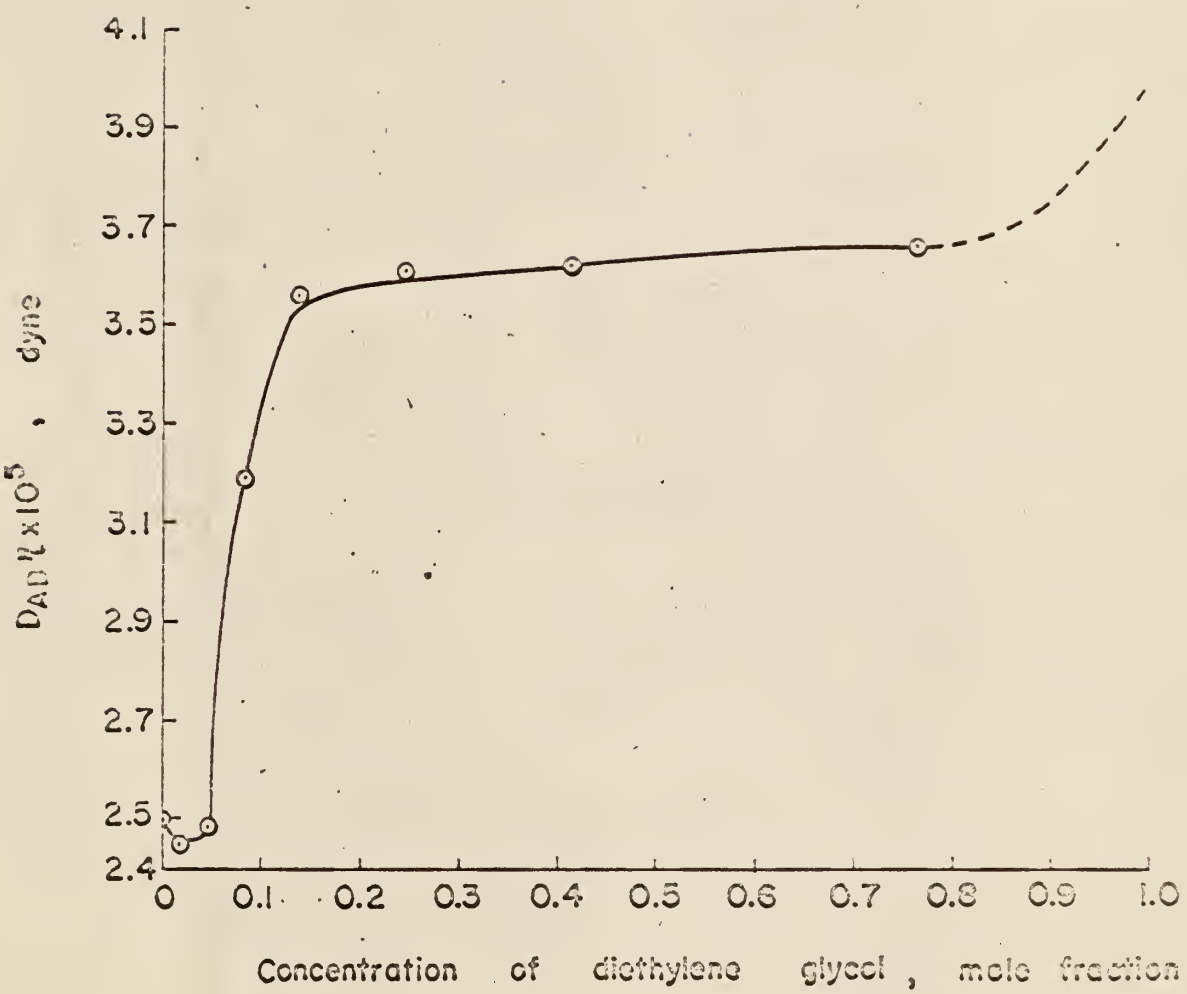


Figure 17 . $D_{AB}\eta$ vs concentration for diethylene glycol-water system at 25° C

effective radius of the molecule which would be a function of concentration. Equation 1 can be rewritten as

$$r_A = \frac{KT}{6 \eta \pi D_{AB}} . \qquad (3)$$

This permits one to calculate r_A which, due to the association or hydration of solute particles (34), varies with composition.

To compare the experimental results with the values predicted by an empirical correlation, the Wilke-Chang correlation (19), equation II-10 reproduced below, is first employed.

$$D_{AB} = 7.4 \times 10^{-8} \frac{(XM)^{\frac{1}{2}} T}{\eta V^{0.6}} \qquad (II-20)$$

where X is association parameter introduced to define the effective molecular weight, M, of the solvent with respect to the diffusion process. V is the molal volume of solute at normal boiling point. Values of D_{AB} are calculated for the whole concentration range and are presented in Table 9 together with experimental values. They are also plotted in Figure 18. Although the Wilke-Chang correlation usually is valid only for very dilute solutions, one can see that in this study of the diethylene glycol-water system, the estimated values of diffusivity for the diffusion of water in the glycol are in fairly good agreement with the experimental values if one takes X = 1.0; for instance, at 50 wt. % water, the deviation is less than 15%. If one adopts X = 2.6 as recommended by Wilke and Chang for the diffusion of diethylene glycol into water, the predicted values of D_{AB} are much less than the experimental values, but the results are in good agreement if one uses a value of 22 for the association parameter, X.

Table 9.

Experimental Diffusivities and the Diffusivities Estimated by the Wilke-Chang Correlation

Concentration wt. % Glycol	Viscosity CP	D_{AB} exp. $\times 10^6$ cm^2/sec	D_{AB} cal. $\times 10^{6+}$ cm^2/sec	Deviation* %	D_{AB} cal. $\times 10^{6‡}$ cm^2/sec	Deviation* %	D_{AB} cal. $\times 10^{6‡}$ cm^2/sec	Deviation* %
100	28.2	1.40	1.38	+ 1.43				
92.23	22.0	1.68	1.77	+ 5.35				
79.35	13.7	2.61	2.84	+ 8.81				
64.54	7.86	4.63	4.95	+ 6.91				
49.96	4.40	7.54	8.84	+14.70	1.96	-74.00	5.70	- 24.40
35.02	2.40	13.20	16.20	+22.72	3.59	-72.80	10.46	- 20.7
19.10	1.30	19.10			6.64	-65.23	19.31	+ 1.09
5.62	0.98	25.0			8.80	-64.80	25.61	+ 2.44
0.00	0.8937	28.0			9.66	-65.59	28.09	+ 0.32

Extrapolated value

+ Water as solute X = 1.0 $D_{AB} = 3.89 \times \frac{1}{\mu} \times 10^{-5}$

‡ Water as solvent X = 2.6 $D_{AB} = 8.63 \times \frac{1}{\mu} \times 10^{-6}$

‡+ Water as solvent X = 22 $D_{AB} = 25.1 \times \frac{1}{\mu} \times 10^{-6}$

* Deviation $= \frac{D_{AB}cal - D_{AB}exp}{D_{AB}\ exp} \times 100$

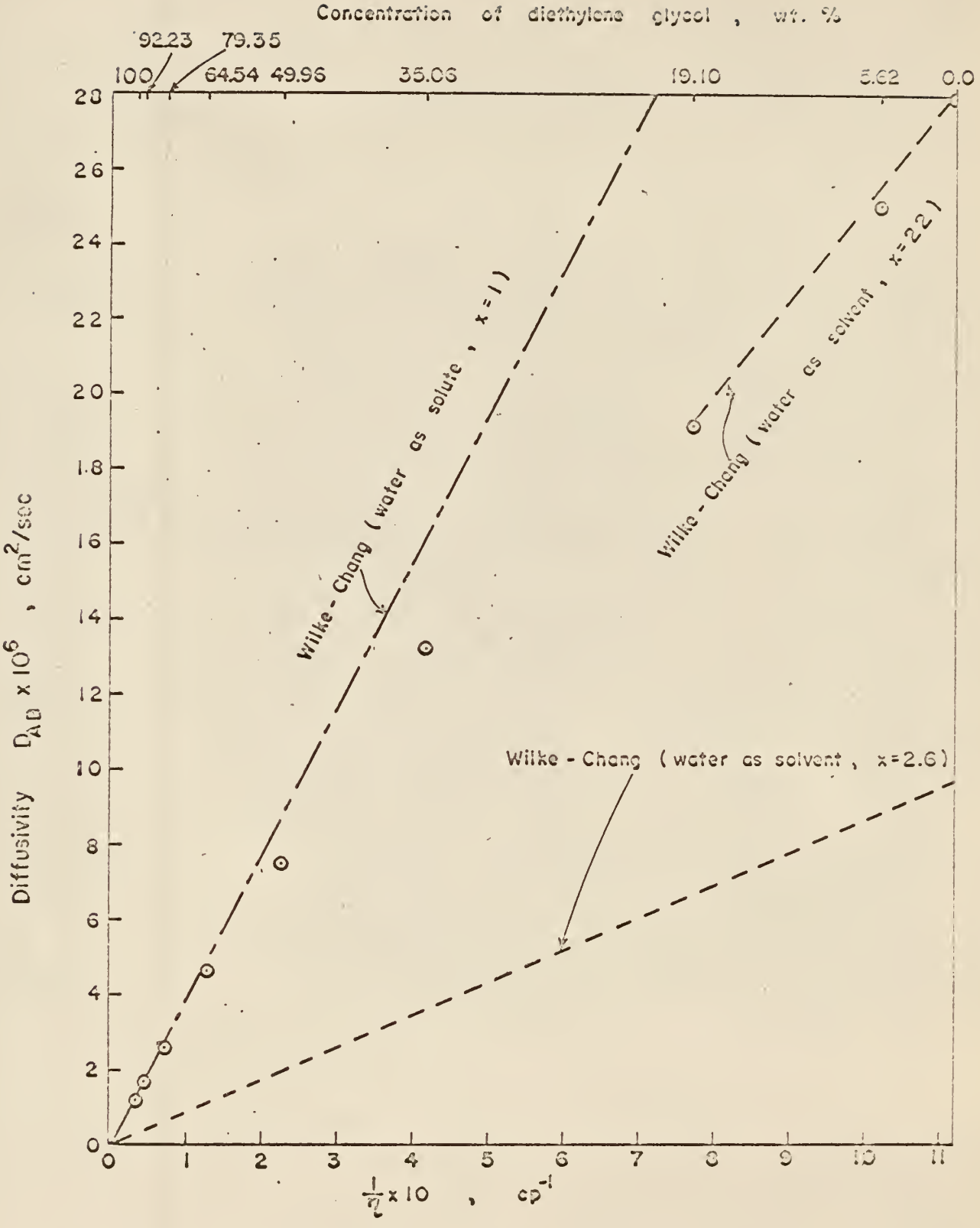

Concentration of diethylene glycol , wt. %
92.23
79.35
100
64.54
49.96
35.06
19.10
5.62
0.0
Diffusivity $D_{AB} \times 10^6$, cm^2/sec
Wilke - Chang (water as solute , x = 1)
Wilke - Chang (water as solvent , x = 2.2)
Wilke - Chang (water as solvent , x = 2.6)
$\frac{1}{\eta} \times 10$, cp^{-1}

Figure 18. Diffusivity vs. $1/\eta$ for diethlene glycol - water system at 25° C

Siraraman, Ibrahim and Kuloor (21) claim that their correlation, equation II-23 reproduced below, holds for the diffusion of water at low concentrations in organic solvents.

$$D_{AB} = 5.4 \times 10^{-8} \left(M_B^{\frac{1}{2}} L_B^{1/3} T / {}_B V_A^{0.5} L_A^{0.3}\right)^{0.93} \qquad \text{(II-23)}$$

The calculated value of D_{AB} from this equation is $6.05 \times 10^{-6} cm^2/sec$. The value is significantly less than the experimental one. The correlation of Othmer and Thaker (20), equation II-22 given below, is also tested for very dilute solution.

$$D_{AB} \times 10^5 = \frac{14.0}{\eta_w (1.1\ L_B/L_w)\ V_A^{0.6}\ \eta_B^o} \qquad \text{(II-22)}$$

The results are shown in Table 10.

Equation (II-14)

$$D_{AB}^o = D_B^o x_A + D_A^o x_B \qquad \text{(II-14)}$$

which states the linear dependence of diffusivities on concentration (23, 24) and the corrected form of this equation, equation II-18,

$$D_{AB}' = (D_B^o x_A + D_A^o x_B) \frac{\eta}{\eta_A x_A + \eta_B x_B} \qquad \text{(II-27)}$$

proposed by MaCall and Anderson (34) are compared with the observed diffusivity of the diethylene glycol system in Figure 19.

The deviations, S^o and S for the linear and corrected curves respectively are given by

Table 10.

Comparison of Methods of Estimating Diffusivities in Infinitely Dilute Diethylene Glycol-Water System at 25°C

Solute (Minor Component)	Solvent (Major Component	$D_{AB} \times 10^6$ cm^2/sec Exp *	$D_{AB} \times 10^6$ cm^2/sec Wilke-Chang	Deviation %	$D_{AB} \times 10^6$ cm^2/sec Othner-Thaker	Deviation %	$D_{AB} \times 10^6$ cm^2/sec Kuloor et. al.	Deviation %
water	Diethylene glycol	1.40	1.38	1.43	0.752	46.28	0.734	47.57
Diethylene glycol	Water	28.0	9.66++	65.5	9.03	67.75	10.18	63.64

* Extrapolated value

$$\text{Deviation} = \frac{D_{AB}\text{cal.} - D_{AB}\text{exp.}}{D_{AB}\text{exp.}} \times 100$$

++ Using X = 2.6

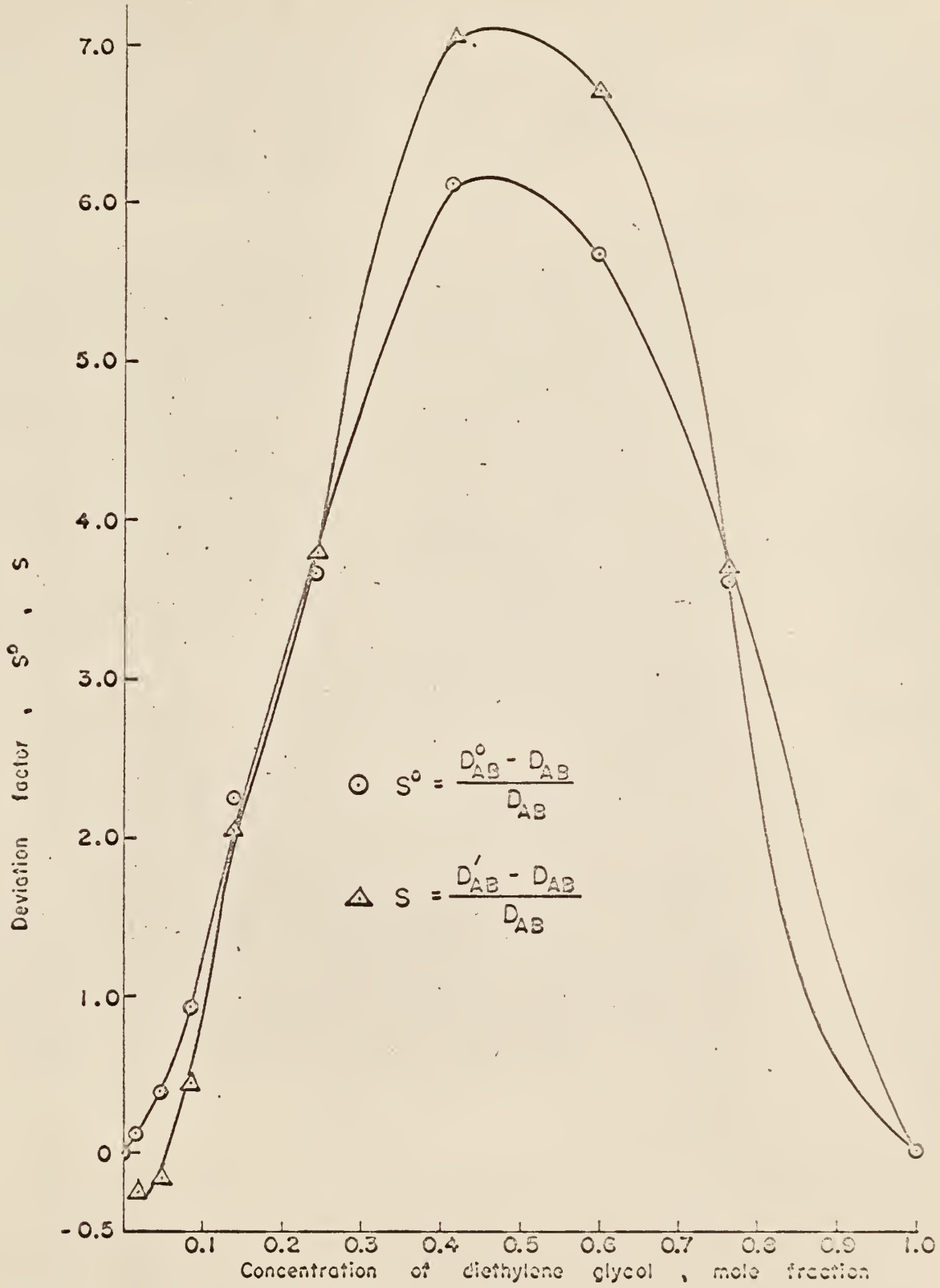


Figure 19. The deviation of diffusivity from a linear function of mole fraction for aqueous diethylene glycol solution

$$S^{o} = \frac{D_{AB}^{o} - D_{AB}}{D_{AB}}$$

$$S = \frac{D_{AB}' - D_{AB}}{D_{AB}} .$$

Clearly neither equation satisfactorily predicts the diffusivity of this system.

From the above comparisons one can conclude that the best predicted values are obtained from the Wilke-Chang correlation with the proper choice of association parameter X, for the diethylene glycol-water system.

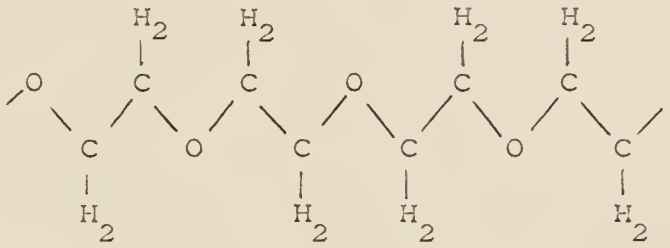
CHAPTER VI

DIFFUSIVITY OF POLYETHYLENE GLYCOL-WATER SYSTEM AT 25 °C

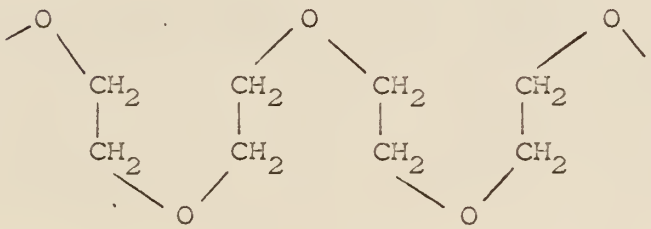
MATERIALS

The polyethylene glycols above triethylene glycol range from water white liquids to wax-like solids. These compounds are water soluble, nonvolatile materials.

Viscosity measurements indicate that the polyethylene oxides exist in two forms (36). The lower polymers poses the ordinary "zig-zag" configuration



while the higher polymers exist in what is termed the "meandering" form



The polyethylene glycol for this investigation was purchased from Matheson, Coleman and Bell Co.. The average molecular weight was 380-400. The material was graded as superior by the manufacturer and was used without further purification. Commercially available polyethylene glycol is actually a mixture of several condensation polymers (37). Some

physical properties of commercially available polyethylene glycol are listed in Table 11 for reference. The solutions were prepared with double-distilled water.

VISCOSITY

Viscosities of polyethylene glycol (M.W. 380-420) were obtained with a Cannon-Fenske routine type viscosimeter and densities were obtained with a 25 cc glass specific gravity bottle. The results are recorded in Table 12 and are also plotted in Figure 20. The viscosities were measured at a temperature of 25 $\pm$ 0.02 ^{o}C

Polyethylene glycol is about 100 times as viscous as water and its viscosity varies inversely with temperature as do most substances. The viscosity composition relationship of the polyethylene glycol-water system is very non-linear.

REFRACTIVE INDEX

The refractive indices of aqueous polyethylene glycol solutions measured with the Bausch & Lomb type Abbe-3L refractometer are summarized in Table 13, and also plotted in Figure 21. Although the refractive index of aqueous polyethylene glycol solution is not a linear function of composition, it can be assumed to be so for small concentration ranges. This is a necessary assumption for deriving equation II-6, repeated below

$$\frac{\partial n}{\partial z} = \frac{n_o'' - n_o'}{2\sqrt{\pi D_{AB} t}} \exp\left(-\frac{z^2}{4 D_{AB} T}\right) . \qquad \text{(II-6)}$$

Table 11.

Physical Properties of Commercially Available Polyethylene Glycol (37)

Average molecular weight	380-420
Freezing range	4-10 °C
Specific gravity 20°C/20°C	1.13
Flash point	435°F (209.7°C)
Saybolt viscosity at 210°F	45-55 sec.
Solubility in water	complete
Comparative hygroscopicity (glcerol = 100	55

Table 12.

Viscosities of Polyethylene Glycol Solutions at 25 °C

Concentration wt. % of glycol	Kinematic viscosity stokes	Density g/ml	Viscosity centipoises
100.0	0.88795	1.115	99.01
90.77	0.71947	1.112	80.00
76.83	0.45027	1.1048	49.74
63.16	0.20686	1.0887	22.52
48.57	0.09298	1.0703	9.95
33.17	0.0396	1.0436	4.132
16.62	0.01844	1.0151	1.87

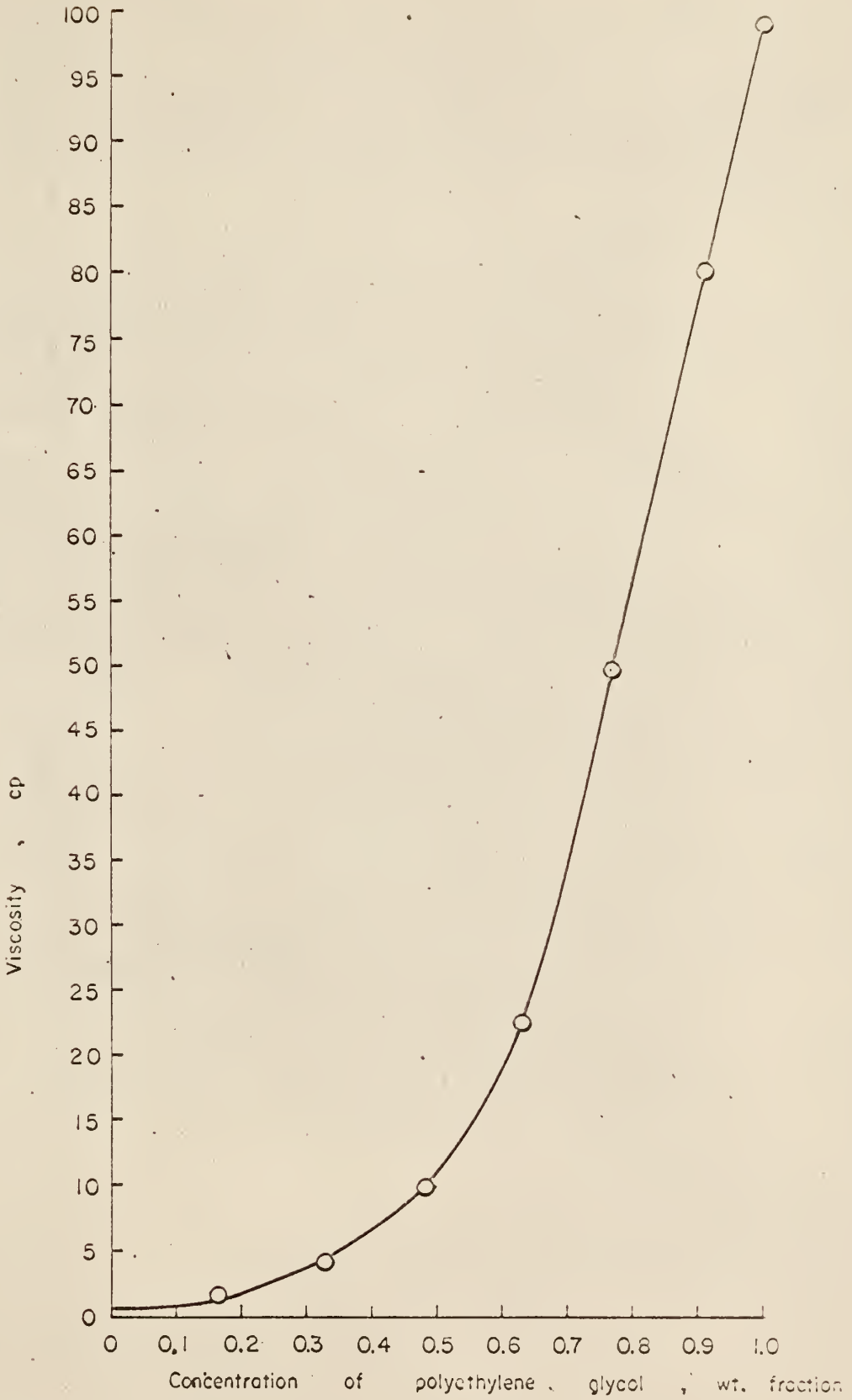


Fig. 20. Viscosity vs concentration for polyethylene glycol-water system at 25°C.

Table 13.

Refractive Index of Polyethylene Glycol and Its Aqueous Solutions at 25 °C

Concentration wt. % of glycol	Refractive index
100	1.4650
86.44	1.4505
72.10	1.4336
57.50	1.4138
42.25	1.3910
26.89	1.3692
11.18	1.3470
0.0	1.3324

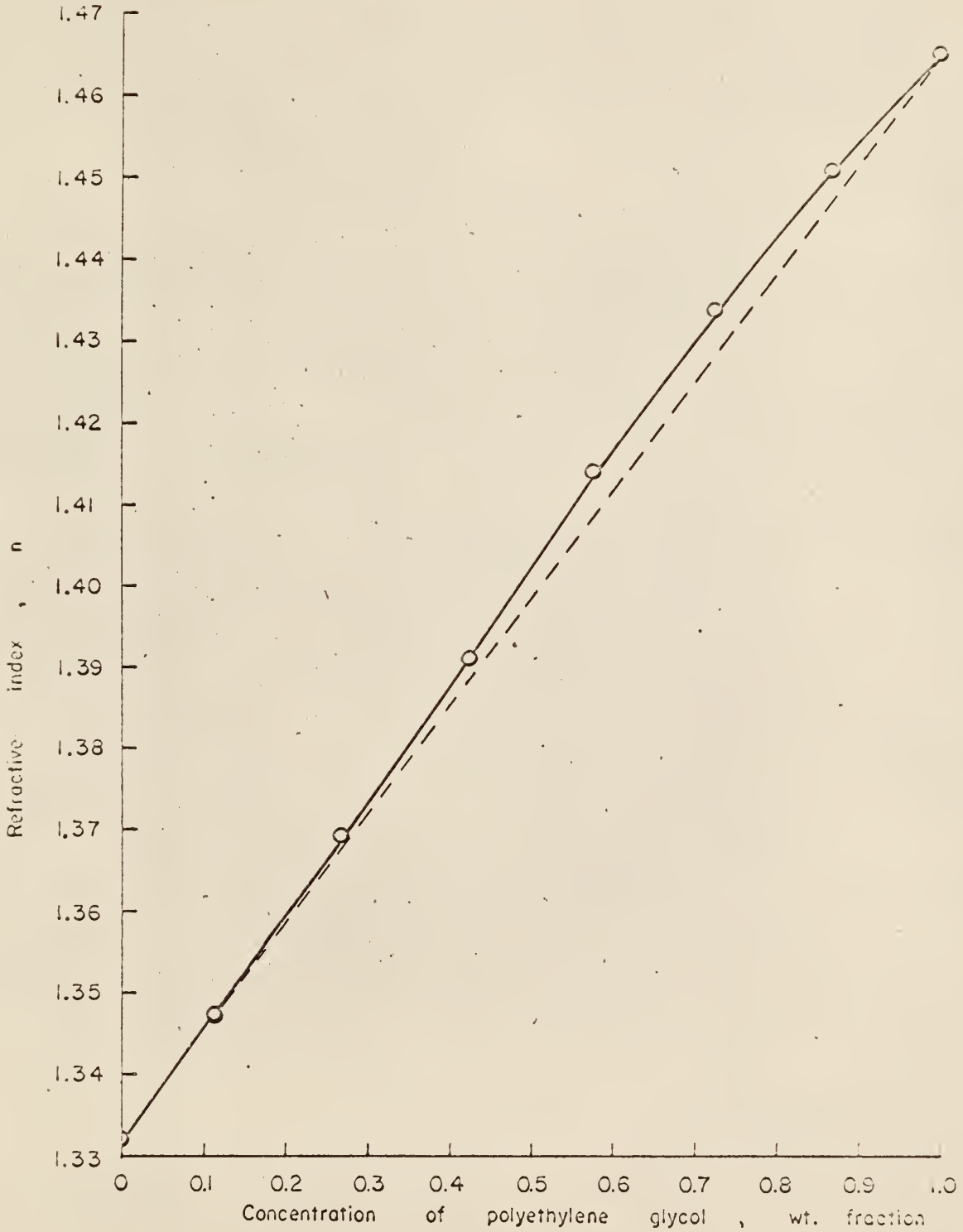


Fig. 21. Refractive indices vs concentration for polyethylene glycol - water system at 25° C.

DIFFUSIVITY

The experimental diffusivities were obtained by measuring the inter-diffusion of two solutions of slightly different concentrations using a micro-interferometric method as described previously. Seven pairs of solutions were measured at atmospheric pressure and at 25 $\pm$ 0.3 ^{o}C. These pairs of solution are:

{ polyethylene glycol
  86.47 wt. % (0.223 mole fraction*) polyethylene glycol solution

{ 86.47 wt. % (0.223 mole fraction) polyethylene glycol solution
  72.10 wt. % (0.104 mole fraction) polyethylene glycol solution

{ 72.10 wt. % (0.104 mole fraction) polyethylene glycol solution
  57.50 wt. % (0.0573 mole fraction) polyethylene glycol solution

{ 57.50 wt. % (0.0573 mole fraction) polyethylene glycol solution
  42.25 wt. % (0.0318 mole fraction) polyethylene glycol solution

{ 42.25 wt. % (0.0318 mole fraction) polyethylene glycol solution
  26.89 wt. % (0.0162 mole fraction) polyethylene glycol solution

{ 26.89 wt. % (0.0162 mole fraction) polyethylene glycol solution
  11.18 wt. % (0.0056 mole fraction) polyethylene glycol solution

{ 11.18 wt. % (0.0056 mole fraction) polyethylene glycol solution
  water

*mole fraction is calculated by assuming average MW = 400

Values of the experimental diffusion coefficients, D_{AB}, and the respective initial and mean concentrations, Co', Co", $\overline{C}$, of the solutions are given in Table 14. Figures 22 and 23 show the concentration dependence of diffusivities. Tables A III-1 through A III-7 in Appendix III give the complete record of the experimental results of this investigation.

Figure 22 shows the diffusivity as a function of weight fraction of polyethylene glycol while the diffusivity is plotted as a function of mole fraction in Figure 23. From these two figures one can see that the diffusivity decreases with increasing glycol concentration. Since viscosity is a measure of internal resistance to the flow of a fluid, the diffusivity should vary inversely with viscosity. This is roughly the case.

For a non-associated solution, ideal or nonideal, $\log(D_{AB})$ usually varies linearly with mole fraction (33). In the case of associated solutions, the exponential variation is found whenever the average degree of molecular association of the associated compound can be considered constant. Log (D_{AB}) is plotted against concentration in Figure 24. It appears that the data can be correlated either by two straight line segments intersecting near the concentration with 0.1 mole fraction of polyethylene glycol or three line segments intersecting at 0.05 and 0.15 mole fractions.

ANALYSIS OF RESULTS

As mentioned previously, no satisfactory theories of the liquid state exist. Consequently no rigorous theories of diffusion for liquids have

Table 14.

Summary of Experimental Diffusivities for Polyethylene Glycol-Water System at 25° C

Initial concentration Co' (glycol)		Co" (glycol)		Average concentration $\bar{C}$ (glycol)		Diffusivity $D_{AB} \times 10^6$
wt. %	mole %*	wt. %	mole %*	wt. %	mole %*	cm^2/sec
100	100	86.44	22.33	93.22	61.16	0.74
86.47	22.33	72.10	10.41	79.27	16.37	0.849
72.10	10.41	57.50	5.73	64.80	8.07	2.21
57.50	5.73	42.25	3.18	49.87	4.45	3.78
42.25	3.18	26.89	1.62	34.57	2.40	11.90
26.89	1.62	11.18	0.56	19.03	1.09	22.80
11.18	0.56	0.0	0.0	5.59	0.28	44.90

* Calculated by assuming average molecular weight of polyethylene glycol = 400.

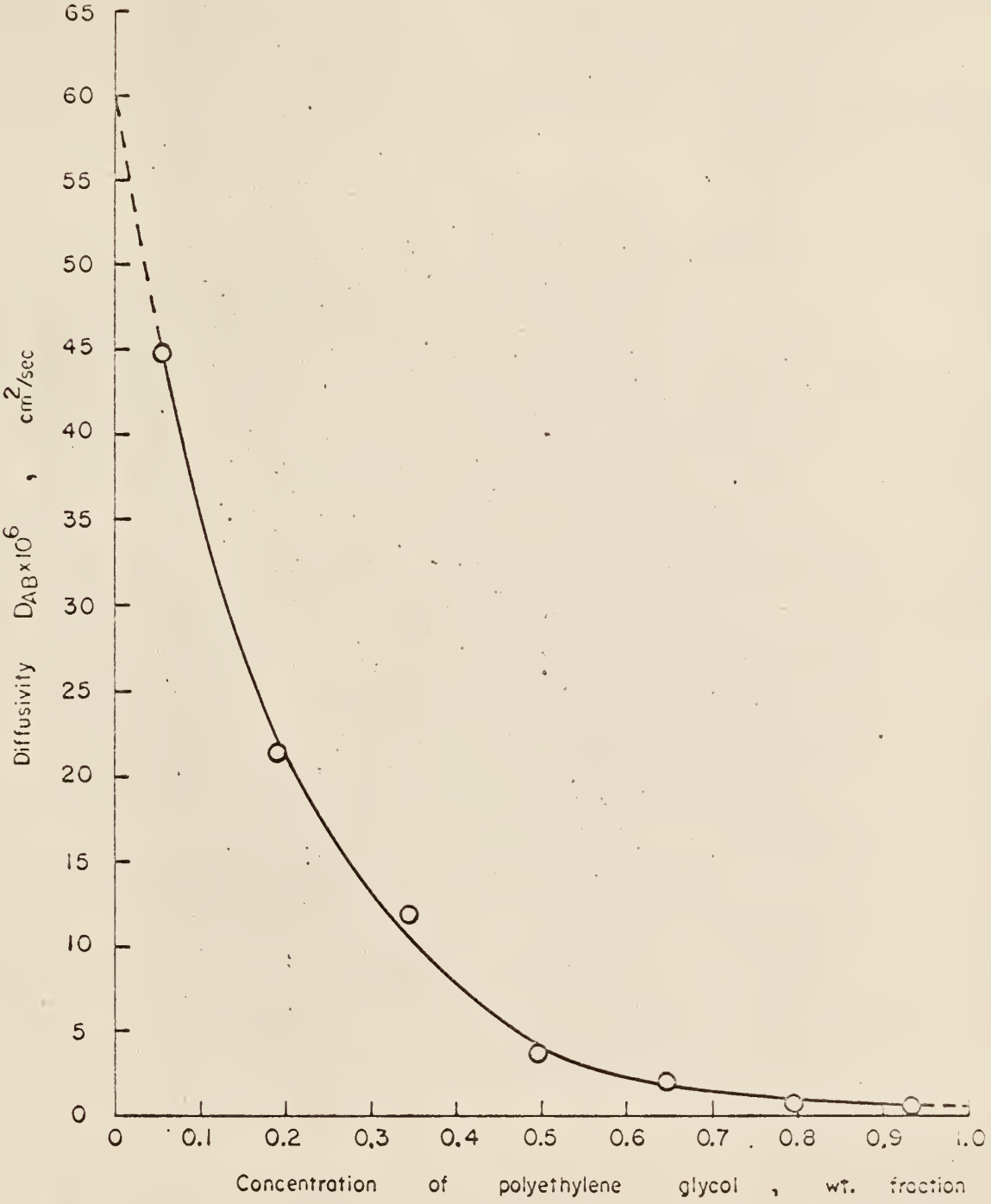


Fig. 22. Diffusivity vs concentration for polyethylene glycol - water system at 25° C.

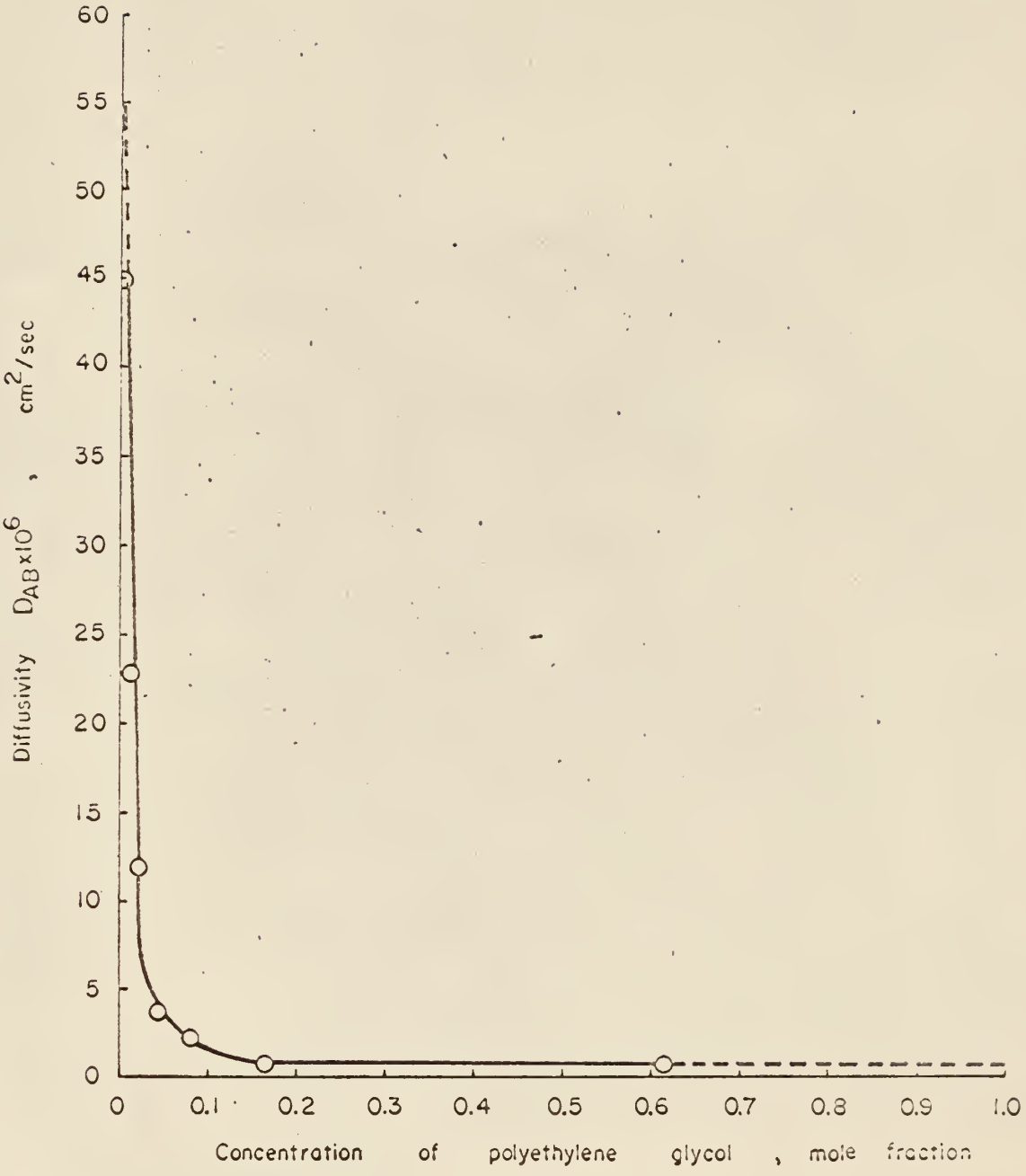


Fig. 23. Diffusivity vs concentration for polyethylene glycol - water system at 25° C.

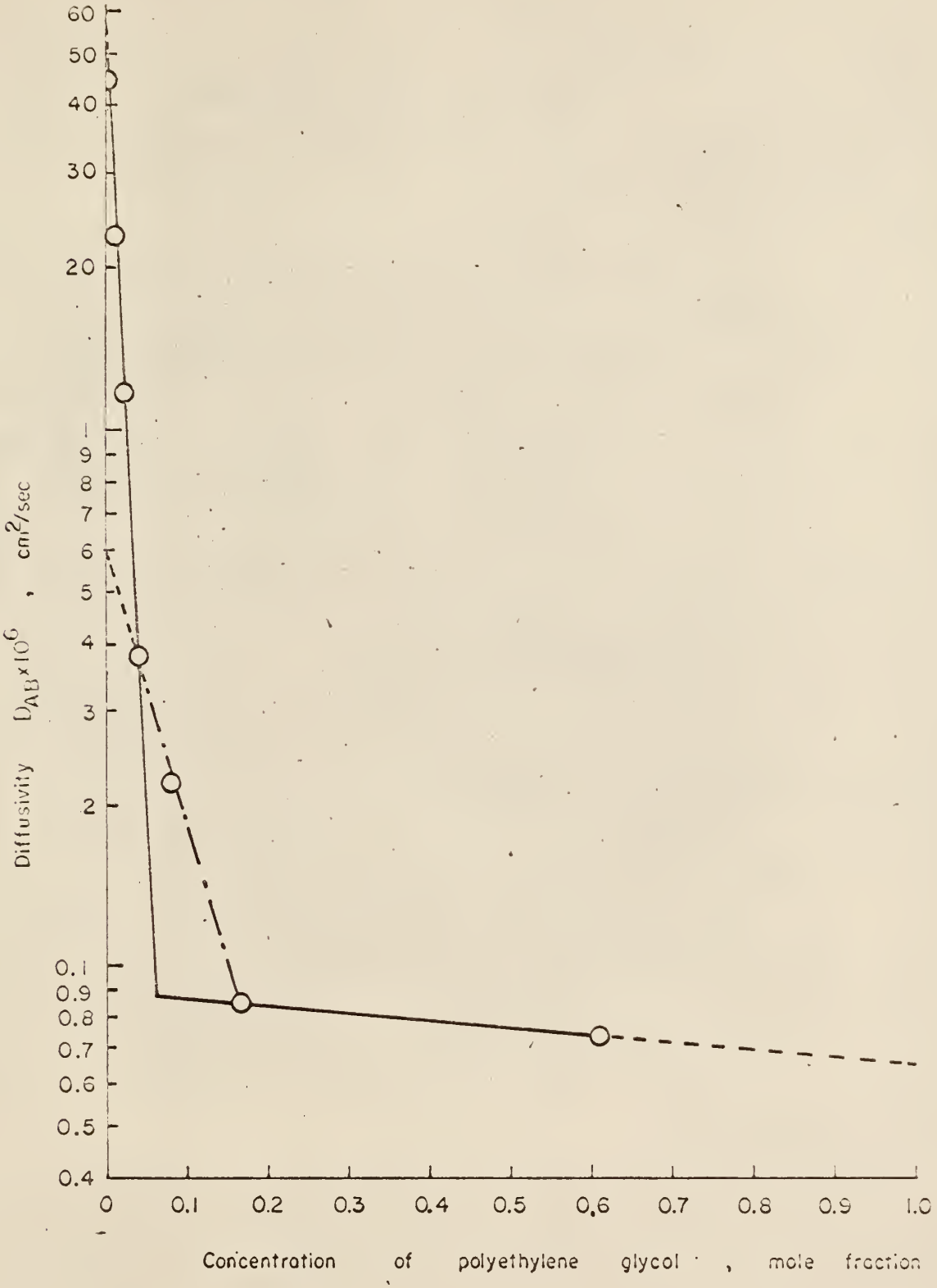


Fig. 24. Diffusivity vs. concentration for polyethylene glycol - water system at 25° C .

been proposed. The hydrodynamic theory which was discussed in chapter II leads to (8, 9)

$$D_{AB} = \frac{K\ T}{6\pi\ \eta_o\ r_A} \qquad (1)$$

which is usually called the Stokes-Einstein equation. Equation 1 may be written in the form

$$D_{AB}\ \eta_o = \frac{K\ T}{6\pi\ r_A} \qquad (2)$$

If the viscosity of solvent, η_o, is replaced by the viscosity of the solution, η, in equation 2, one can see that at constant temperature, $D_{AB}\eta$ should be a constant in the whole concentration range if the molecular radius, r_A, of the solute can be assumed constant. A plot of $D_{AB}\eta$ vs concentration is shown in Figure 25. From this figure, one can see that the value of $D_{AB}\eta$ oscillates considerably. Since commercially available polyethylene glycol is actually a mixture of several condensation polymers one cannot expect the value of $D_{AB}\eta$ remain constant in the whole concentration range. However, as one can see, variation of $D_{AB}\eta$, ranging from the value of approximately 41 to 62, is much less drastic than those of D_{AB} and η alone. An extension of this theory gives rise to the definition of an effective radius of the molecule which would be a function of concentration. Equation 1 can be rewritten as

$$r_A = \frac{K\ T}{6\pi\ \eta\ D_{AB}} \qquad (3)$$

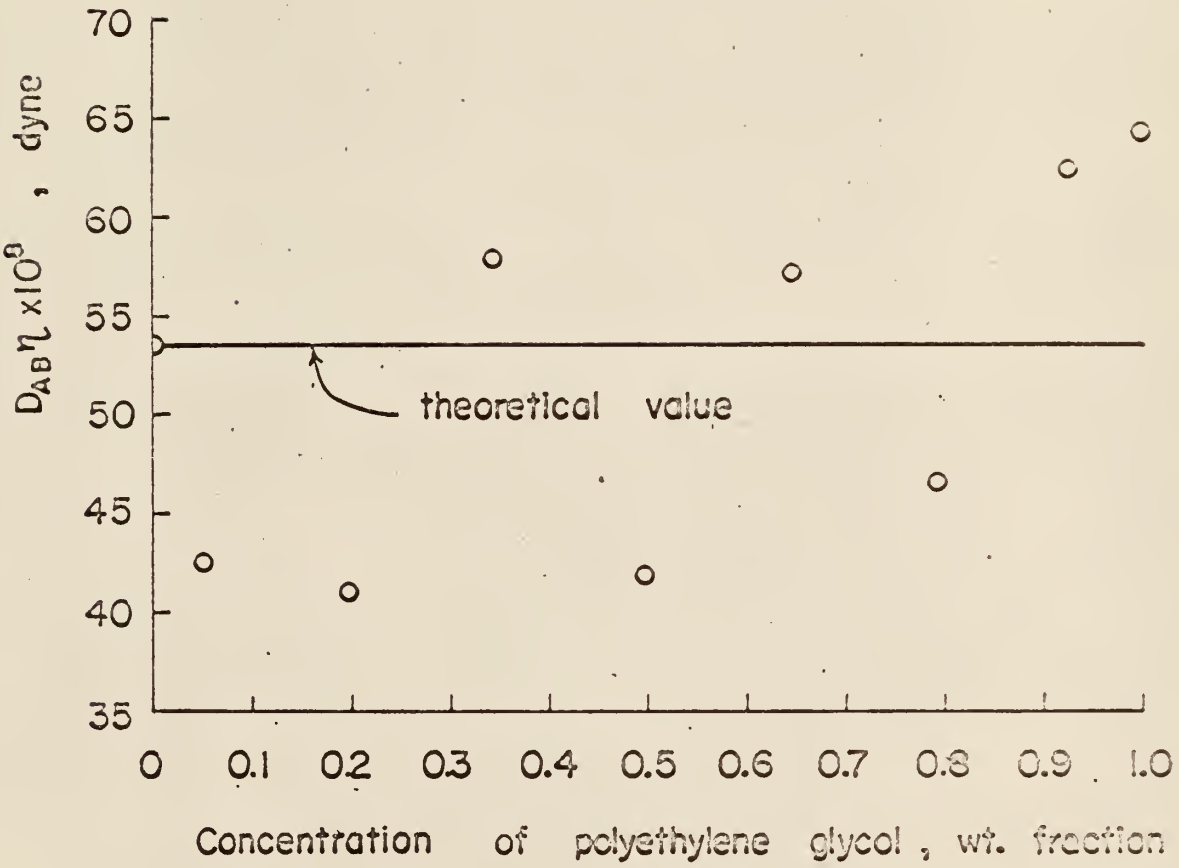


Fig. 25. $D_{AB}\eta$ vs concentration for polyethylene glycol-water system at 25°C.

This permits one to calculate r_A which, due to the association or hydration of solute molecule, varies with composition (33).

To compare the experimental results with the values predicted by an empirical correlation by Wilke and Chang (19), equation II-20 reproduced below, is first employed.

$$D_{AB} = 7.4 \times 10^{-8} \frac{(XM)^{\frac{1}{2}} T}{\eta V^{0.6}} \qquad (4)$$

where X is the association parameter introduced to define the effective molecular weight of the solvent with respect to the diffusion process. M is the molecular weight of the solvent, V is the molal volume of solute at the normal boiling point. Adopting X = 1.5 as proposed by Sherwood and Reed (38) for the ethylene glycol-water system and V = 18.54 cc/g-mole for water, the calculated value of D_{AB} for water diffusing into polyethylene glycol (at infinite dilution of water concentration) is 0.78×10^{-6} cm^2/sec. The corresponding experimental result (extrapolated value) is 0.65×10^{-6}. In calculating D_{AB} the molecular weight of solvent, i.e., polyethylene glycol, was taken to be 400. The diffusivity of polyethylene into water at infinite dilution was not calculated since the commercially available polyethylene is a mixture and the molal volume at the normal boiling is not available.

Equation II-24

$$D_{AB} = D_B^{\circ} X_A + D_A^{\circ} X_B$$

which states the linear dependence of diffusivities on concentration (23, 24) and the corrected form of this equation, equation II-27

$$D_{AB}' = (D_B^{\circ} X_A + D_A^{\circ} X_B) \frac{\eta}{\eta_A X_A + \eta_B X_B}$$

proposed by MaCall and Anderson (35) are compared with the observed diffusivity of the polyethylene glycol system in Figure 26. The deviations, S° and S, for the linear and corrected curves respectively are given by

$$S^{\circ} = \frac{D_{AB}^{\circ} - D_{AB}}{D_{AB}}$$

$$S = \frac{D_{AB}' - D_{AB}}{D_{AB}}$$

Figure 26 clearly shows that neither equation II-24 nor equation II-27 satisfactorily predicts the diffusivity of this system.

Plausible reasons that the semilog plot of D_{AB} against mole fraction yields approximately two or three straight line segments as shown in Figure 5 are listed below:

(1) A drastic change in degree of association or liquid structure due to the hydrogen-bonding of water molecules to the hydroxyl group of polyethylene glycol may take place by going from the one concentration range to the other (39).

(2) The polyethylene glycol used is not a pure material but is a mixture as mentioned previously.

(3) At a lower concentration of polyethylene glycol, the viscosities are very low compared to those at the higher concentration range as can be seen in Figure 20. When the viscosity becomes lower, the bulk mixing effect caused by the initial contact velocity when pressing the two drops of solution in the cell into contact becomes very appreciable,

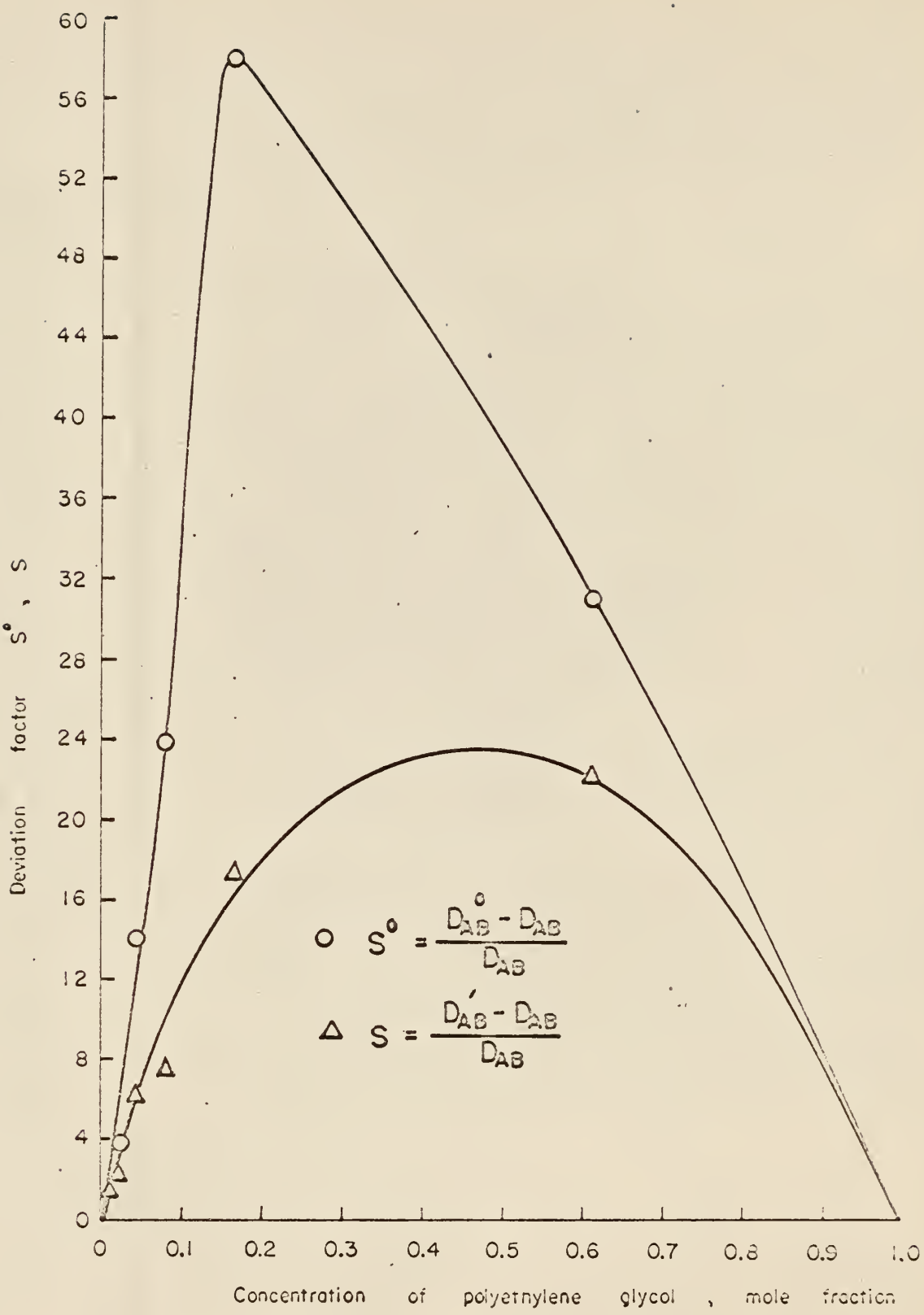


Fig. 26. The deviation of diffusivity from a linear function of mole fraction for aqueous polyethylene glycol solution.

and this will increase the diffusivity to an abnormally high value.

CHAPTER VII

ANALYSIS OF THE RESULTS OF THE FOUR GLYCOL-WATER SYSTEMS AND CONCLUSION

Glycols are those compounds having two hydroxyl (-OH) groups attached to separate carbon atoms in an aliphatic carbon chain. The simple glycols are stable, odorless, water-white liquids. They have higher boiling points than water. The lower glycols are completely soluble in water and the solubility decreases with increasing molecular weight. The lower glycols are extremely hygroscopic. As the molecular weight increases, the freezing or melting point, specific gravity, flash point, and viscosity increase, while vapor pressure and hygroscopicity decrease. Some physical properties of ethylene, diethylene, triethylene and polyethylene glycols are listed in Table 15.

VISCOSITY OF GLYCOL-WATER SYSTEMS

The viscosities of the four glycol-water systems investigated are plotted against concentration in Figures 27 and 28. Viscosity data of ethylene and triethylene glycol solutions were measured by Jerome (2) and those of polyethylene glycol solutions were measured by the author. In Figure 28, the viscosity values for aqueous ethylene glycol solutions interpolated from the data published by the National Bureau of Standards (41) giving the viscosity of pure ethylene glycol and its aqueous solutions from -50 to 350 ^{o}F are also plotted for comparison. The estimated viscosities of aqueous ethylene and triethylene glycol solutions from the viscosity-concentration curve (no data given) published by Dow Chemical Co. (40) are also plotted in Figure 28. As can be seen from the figure

Table 15.

Physical Properties of the Glycols (40)

Name	Formula	Molecular Weight	Apparent specific gravity 20°C/20°C	Boiling point at 760 mm Hg °C	Freezing point °C
Ethylene glycol	CH_2OHCH_2OH	62.07	1.1155	197.2	- 13
Diethylene glycol	$O(CH_2CH_2OH)_2$	106.12	1.1184	245.0	- 8
Triethylene glycol	$HOC_2H_4OC_2H_4$	150.17	1.1254	287.4	- 7.2
Polyethylene glycol		380-420	1.13		4-10

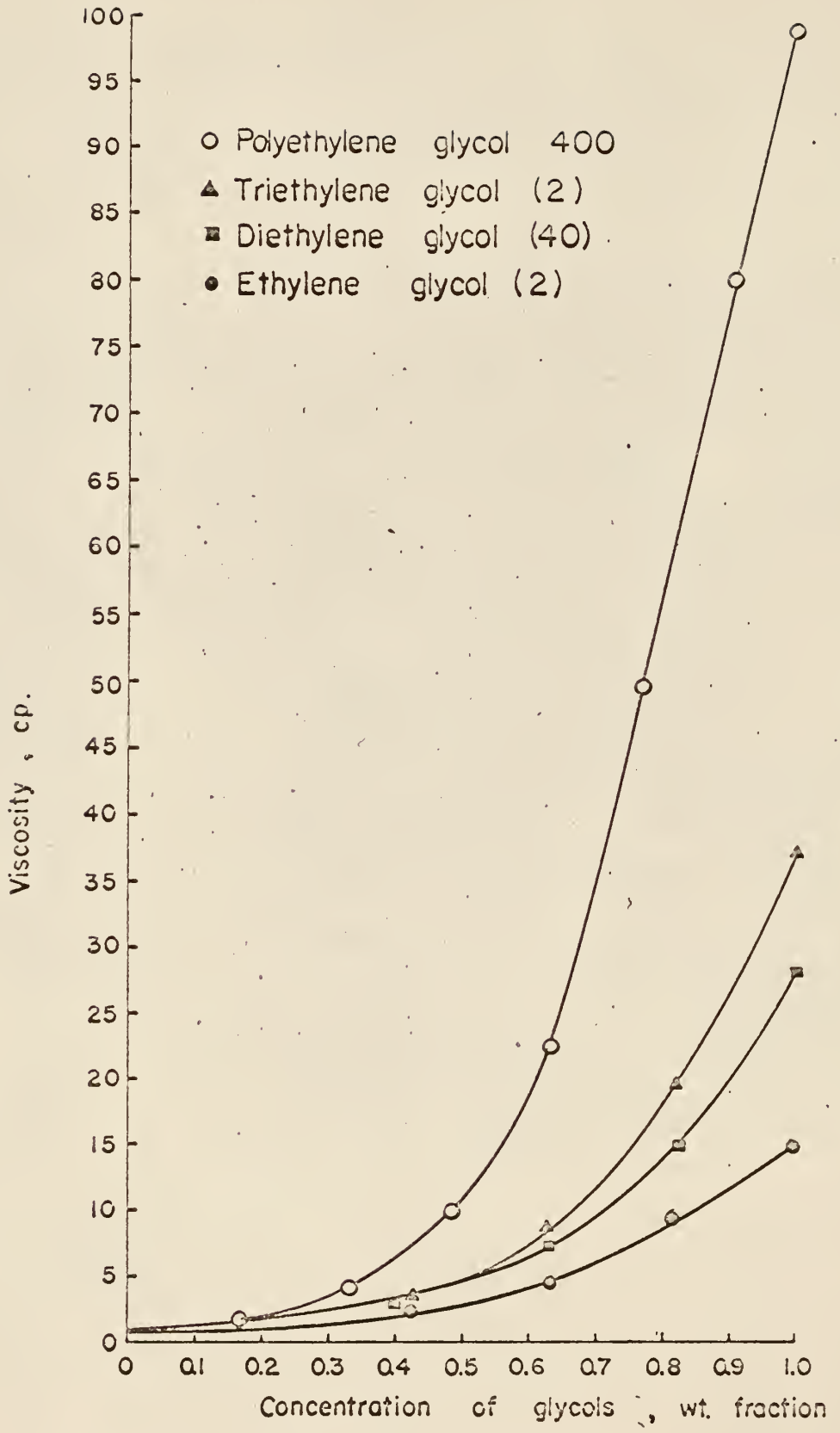


Figure 27. Viscosity vs concentration for mono, di, tri & polyethylene glycols-water system at 25°C.

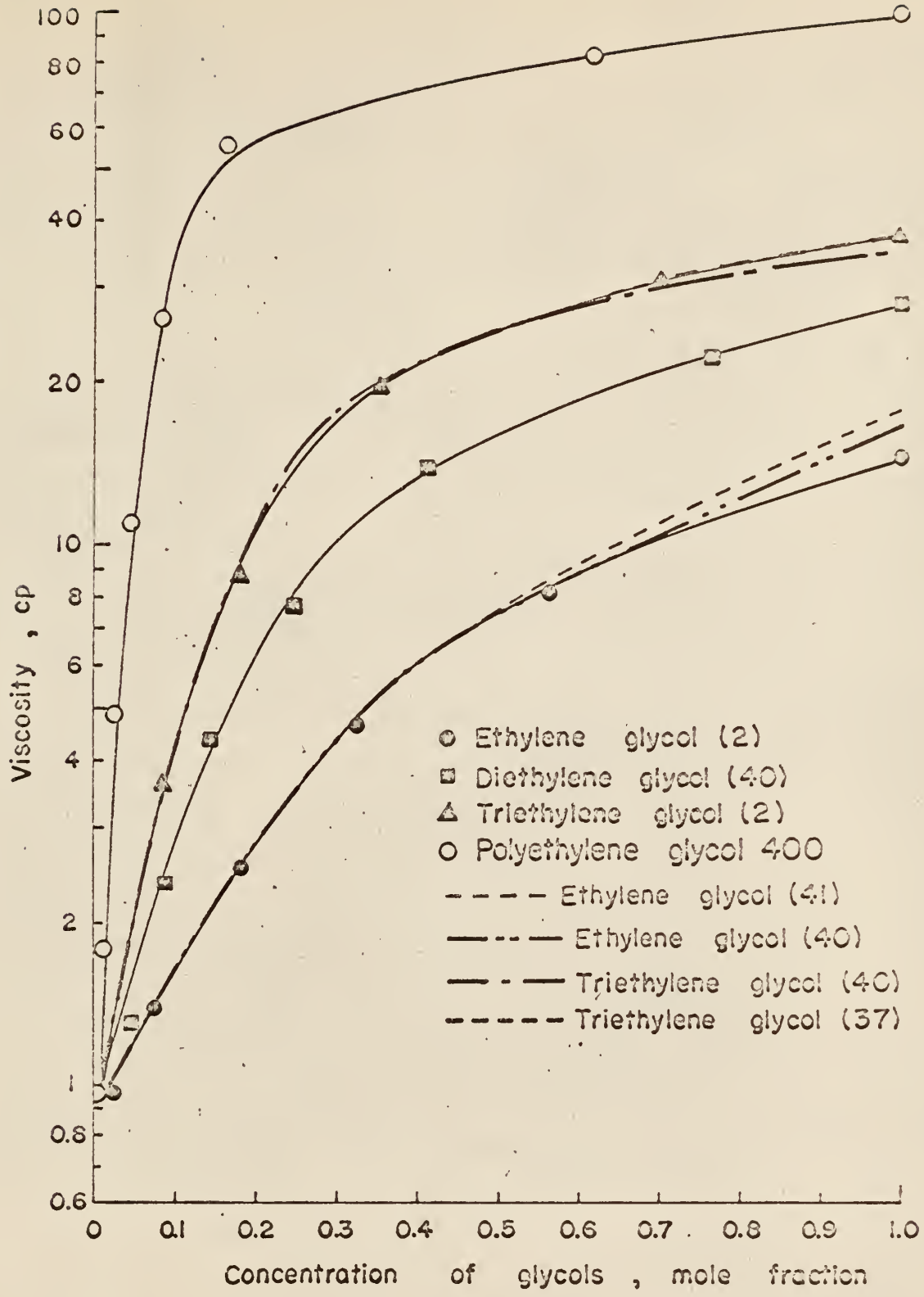


Fig. 28. Viscosity vs. concentration for glycol-water systems at 25°C.

at high concentration Jerome's data appear to be slightly lower than Dow data. For triethylene glycol solution Jerome's data are in close agreement with the Dow data estimated from the figure published by Dow Chemical Co. In Figure 28 the viscosity data of triethylene glycol solutions estimated from the figure presented in "Glycols" by Curme (37) are also shown. The values are slightly higher than that of Jerome's at high concentration end. As can be seen from Figure 27 and 28, fairly drastic changes of viscosities occur at a concentration approximately between 0.1 and 0.4 mole fraction of glycols. When log (η) is plotted against mole fraction as shown in Figure 28 the slope increases with increasing molecular weight of glycols at the low concentration end, while the slope does not have a significant change at the high concentration range and the curves show a fairly drastic change in slope at approximately 0.4 mole fraction for ethylene glycol; 0.25 for diethylene glycol; 0.2 for triethylene glycol; and 0.1 for polyethylene glycol. The ratio of the number of molecules of glycol to that of water, i.e., the molar ratio, can be computed from the concentration expressed in mole fraction; the molar ratio of water to glycol at the breaking point increases with increasing chain length of glycols. This may indicate that the number of water molecules hydrogen-bonded to a glycol molecule increases with increasing molecular weight of glycols. Above a certain concentration, a large fraction of molecules become hydrogen-bonded to the glycol molecule and hence the viscosity does not increase too much when the mole fraction becomes higher.

The viscosities of glycols and their aqueous solutions are plotted against the molecular weight of glycols at several concentrations in Figure 29. The increment of viscosity with molecular weight is small at

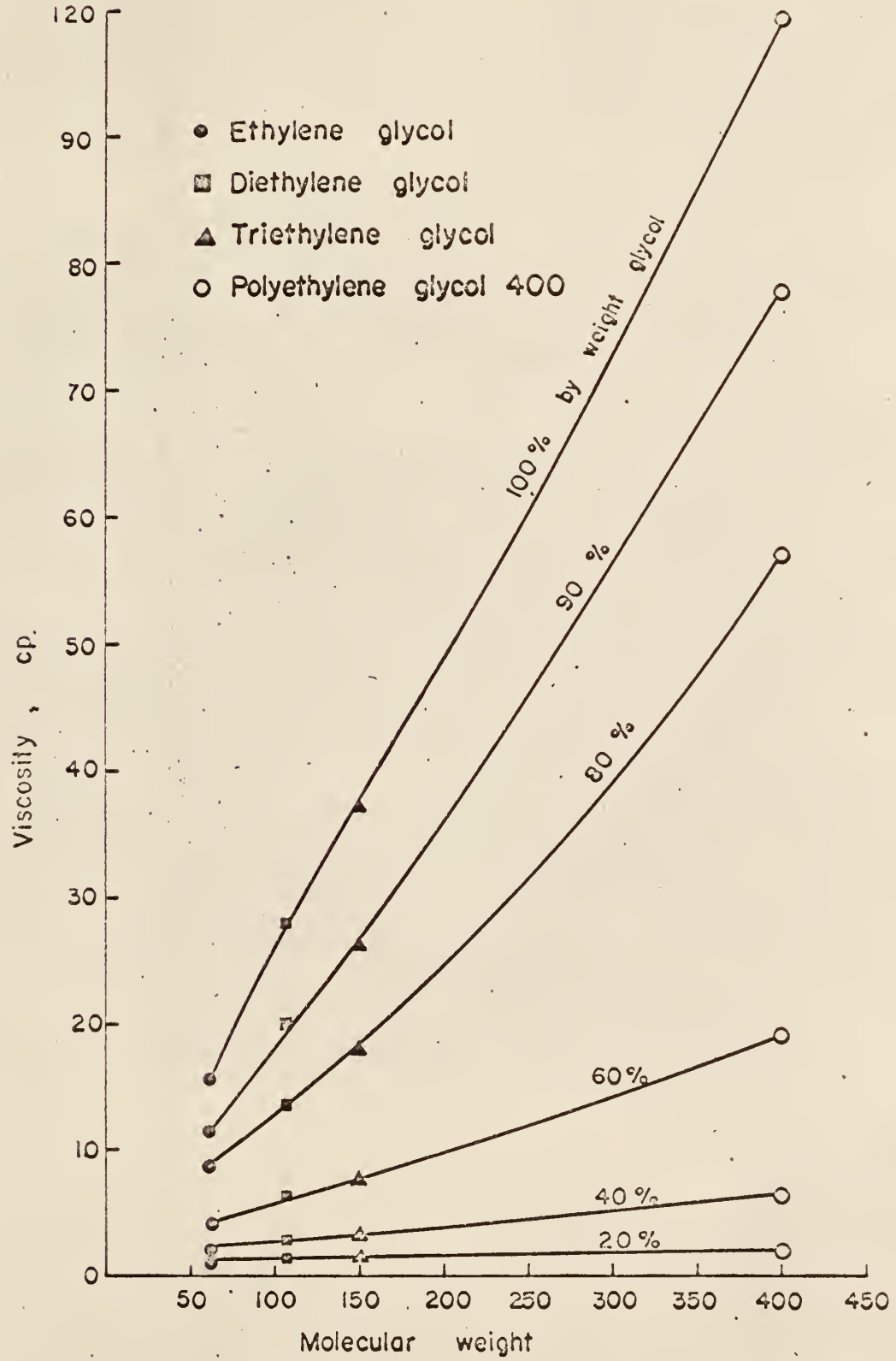


Figure 29. Viscosity of glycol-water systems vs. molecular weight of glycols.

low concentration and increases more quickly when the concentration becomes higher.

REFRACTIVE INDICES OF AQUEOUS GLYCOL SOLUTIONS

The refractive indices of aqueous glycol solutions were measured at 25 ^{o}C. Data for ethylene and triethylene glycol solutions were obtained by Jerome (2) and those for aqueous diethylene and polyethylene glycol solutions were observed by the author. The refractive indices of pure glycols increase with increasing molecular weights of glycols. For aqueous glycol solutions the refractive indices vary almost linearly with composition except at the high concentration end where the curve becomes slightly convex. The results are shown in Figure 30. These results are in good agreement with the values estimated from the refractive index-concentration figures published by Dow Chemical Co. In this work the refractive index is assumed to vary linearly with composition; therefore, it is desirable to choose a small concentration difference in the higher concentration range in making a diffusion run to satisfy this assumption.

DIFFUSIVITY AND CONCENTRATION

In Figures 31 and 32 diffusivities D_{AB} of the four glycol-water systems are plotted against wt. fraction and mole fraction of glycol respectively. The semilog plot of diffusivity shows that the curvature for the ethylene glycol-water system is less pronounced than those for the other system and can be represented approximately equally well by either a straight line or two straight lines. The curves for other systems have sharp breaks at the mole fraction of glycol between 0.1 and

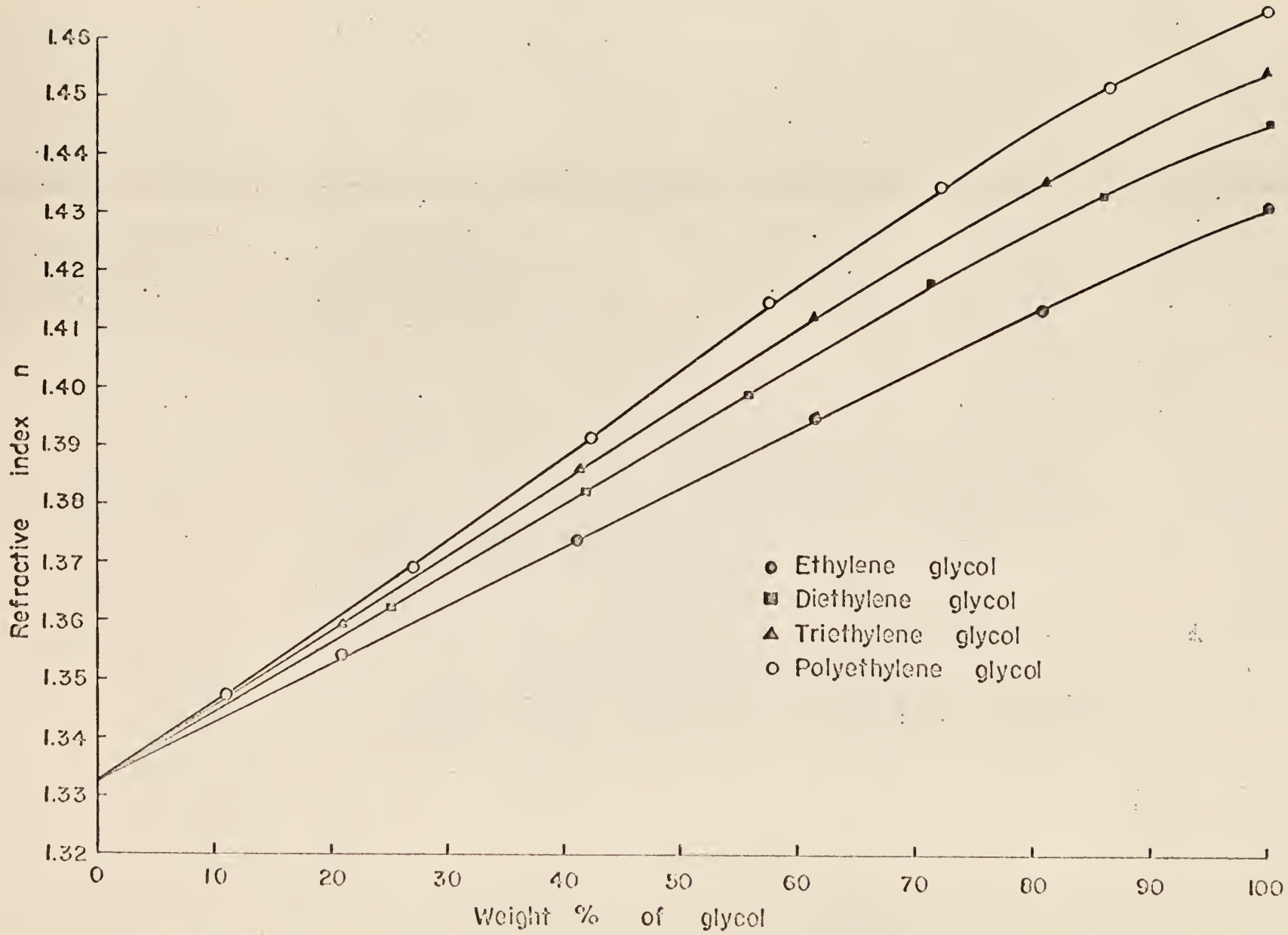


Fig.30. Refractive indices of aqueous glycol solutions at 25 °C .

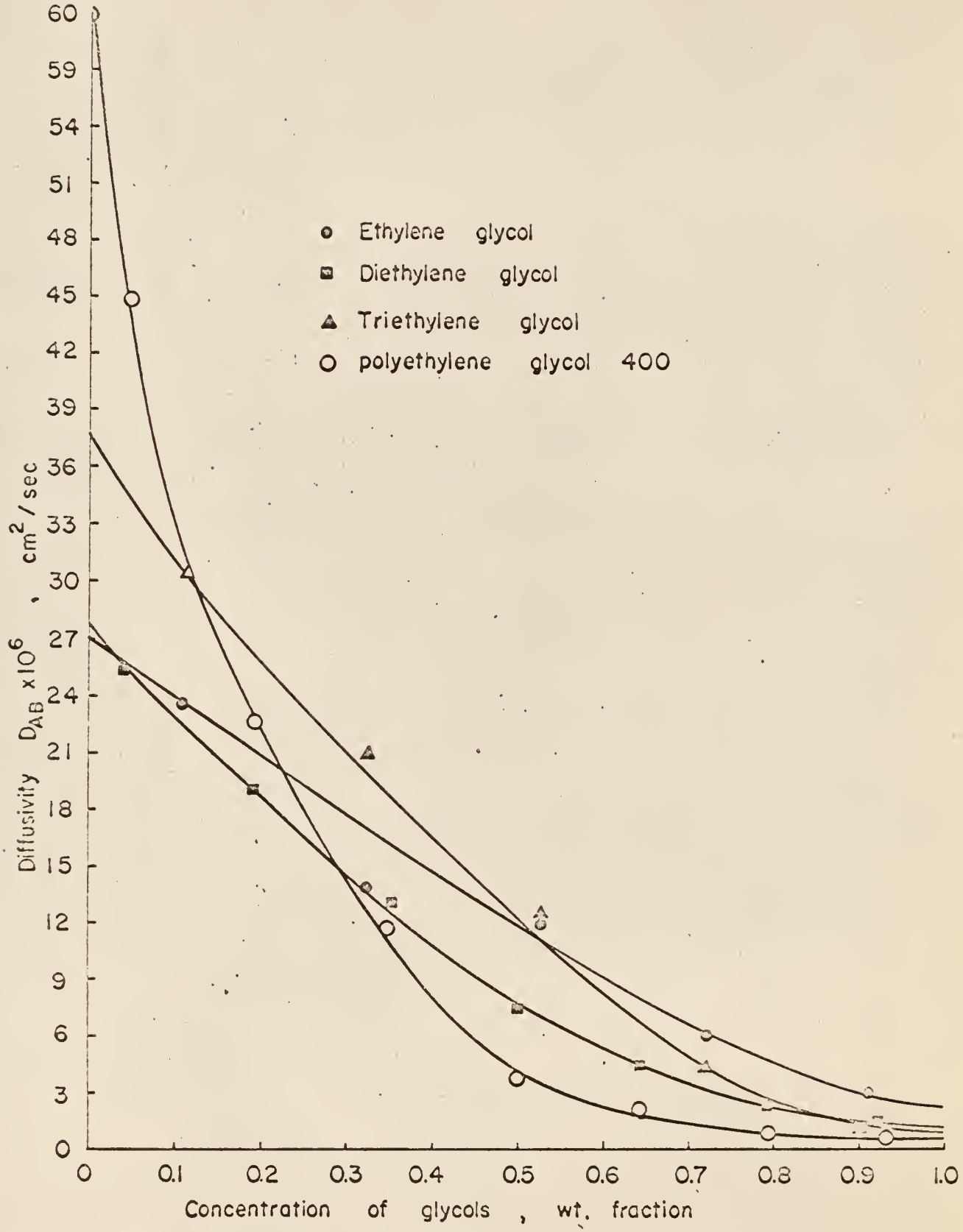


Figure 31. Diffusivity vs concentration for aqueous glycol solution at 25 °C.

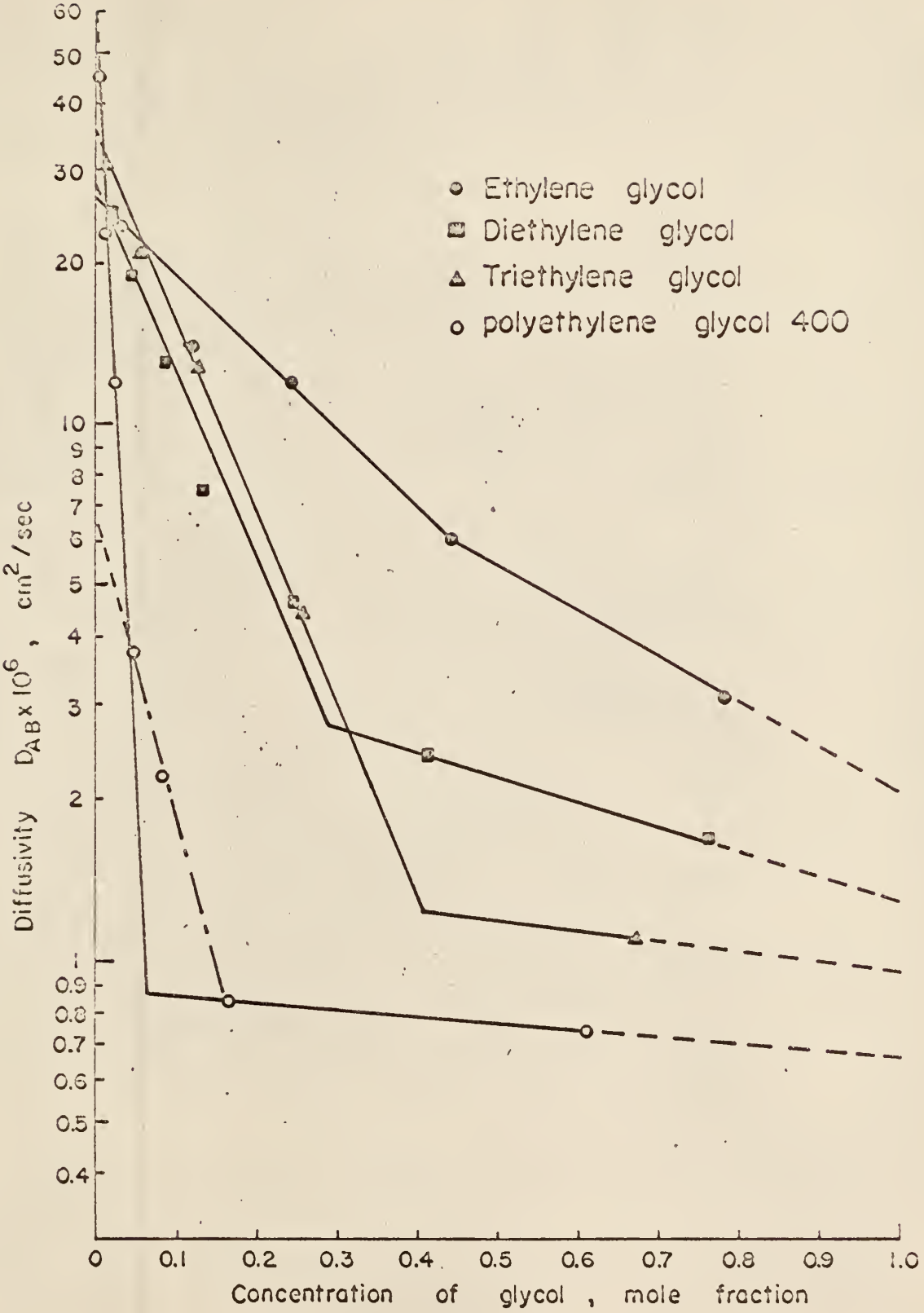


Figure 32. Diffusivity vs concentration for four glycol-water systems at 25°C.

0.3 and can be represented roughly by two straight line segments for each system. The breaking points of these curves nearly coincide with those of the viscosity curves. The diffusivities are much less concentration dependent at a high concentration range than at a low concentration range of glycol. As discussed in the previous section, at the higher concentration range of glycol, water molecules tend to be hydrogen-bonded to the hydroxyl group or groups of the glycol molecules and these resulting complexes diffuse through water. At the lower concentration range of glycol, glycol molecules diffuse through water.

In each of these four systems the diffusivity decreases with increasing concentration of the more viscous component, i.e., glycol. The diffusivity falls steeply when glycol is added to water. At the high concentration end diffusivities decrease with increasing molecular weight of the glycols while at the lower concentration end they increase with increasing molecular weight. The latter cannot be explained rationally. The reliability of the diffusivity data in the low concentration regions of glycols will be discussed in a later section.

REFERENCE SUBSTANCE PLOT OF DIFFUSIVITY

For the exponential variation of diffusivity against concentration, D_{AB} can be generally represented by the following equation

$$D_{AB} = k \exp(-aC_A) \qquad (2)$$

where k and a are constants and C_A is the concentration of the diffusing molecule in mole fraction. Taking logarithms and differentiating

$$d \log(D_{AB}) = -a \, dC_A \, . \qquad (3)$$

This suggests that a linear plot will result if log (D_{AB}) as the ordinate is plotted against log (D_{AB}) for the reference substance as the abscissa. In Figure 33 ethylene glycol is chosen as the reference substance. Again, this gives rise to two approximately straight line segments for each plot.

DIFFUSIVITY-VISCOSITY PRODUCT, $D_{AB}\eta$, AND MOLAR CONCENTRATION

The Stokes-Einstein equation, equation II-12, states that if a rigid spherical molecule of radius r_A diffuses through a solvent of viscosity η , the product of diffusivity D_{AB} and viscosity η is a constant, i.e.,

$$D_{AB}\eta = \frac{kT}{6\pi r_A}$$

under the condition of constant temperature.

Equation 1 was tested with the diffusivity and viscosity data for each of the four aqueous glycol solutions as shown in Figure 34. From this figure one can see that none of the four systems has a strict constant diffusivity-viscosity product over the complete range of concentration. Comparison of the curves indicates the variation of D_{AB} is more irregular for higher molecular weight glycols than for lower molecular weight glycol. This irregular variation is very pronounced for polyethylene glycol 400. Since it is actually a mixture of several condensation polymers, the wide deviation of $D_{AB}\eta$ of polyethylene glycol is not unexpected.

Though the value of $D_{AB}\eta$ varies considerably with concentration, the variation is not so drastic compared to the variation of the value of

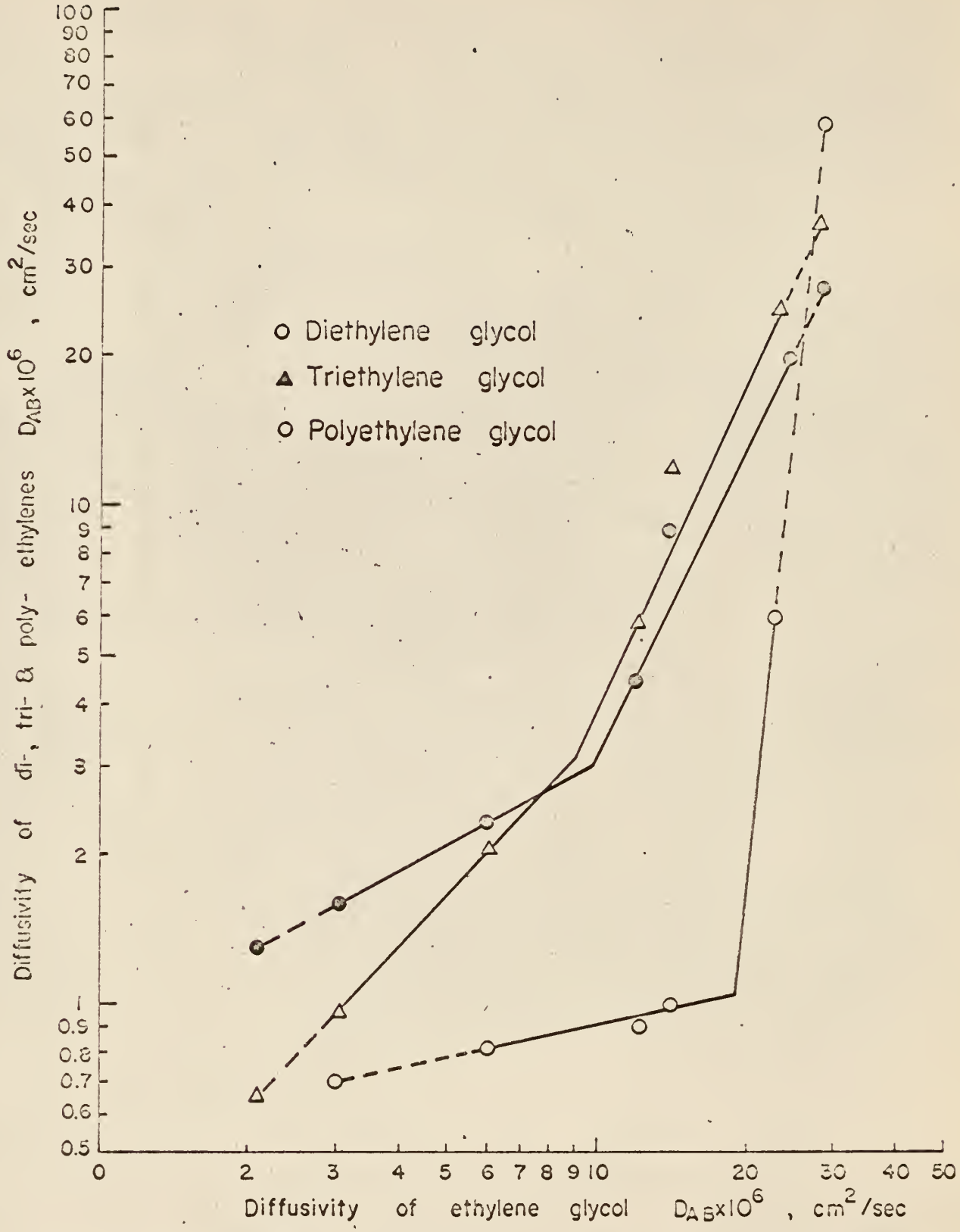


Figure 33. Reference substance plot for the diffusivities of glycol - water systems at 25 °C.

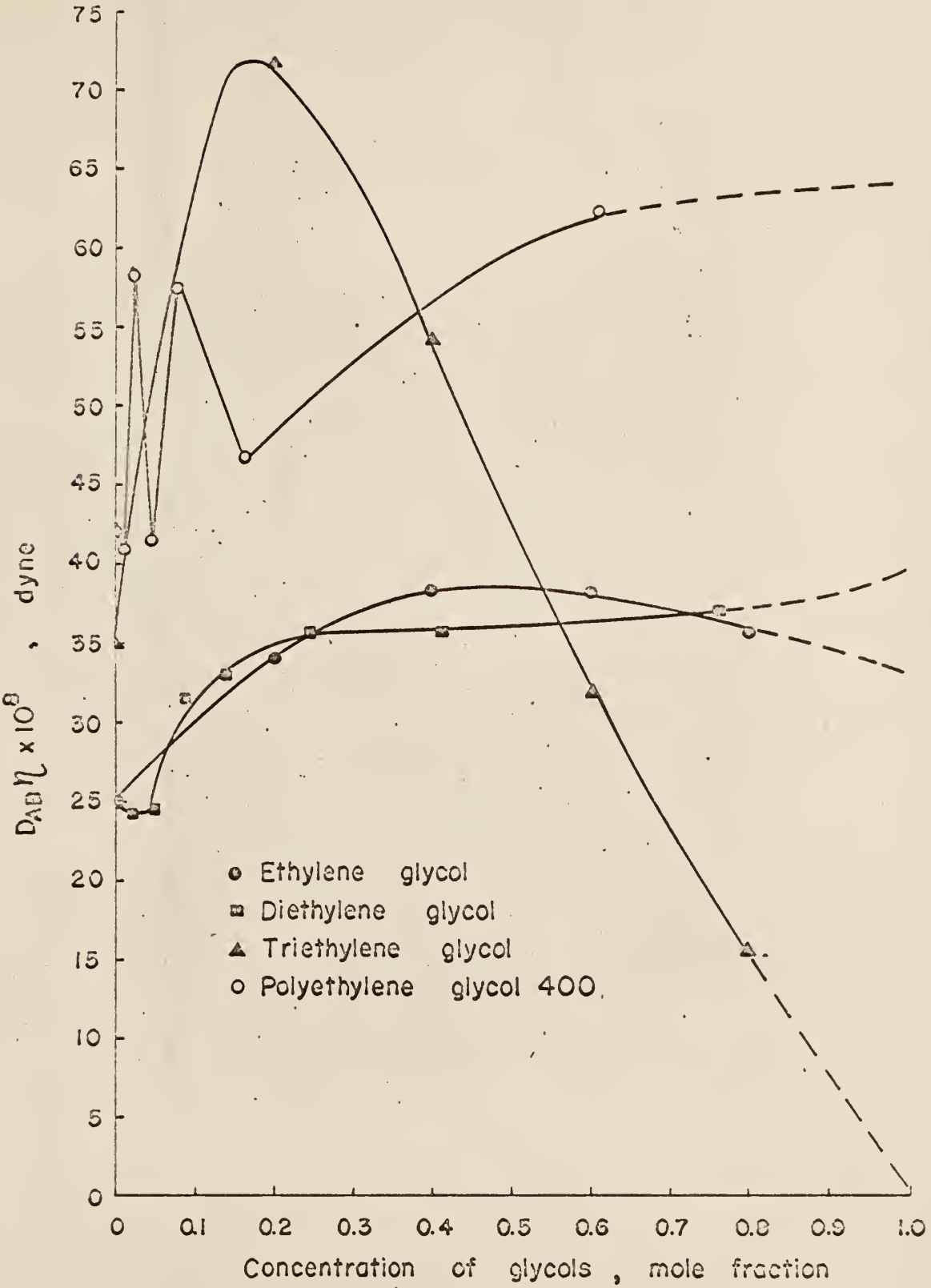


Fig.34. The products of diffusivity and viscosity for aqueous glycol solutions at 25 °C .

D_{AB} or η alone. For example, the value of $D_{AB}\eta$ of the polyethylene glycol solution changes approximately from 40 to 65 while the value of D_{AB} changes almost 70 fold ranging from 0.7 to 60 and that of η changes from 0.9 to 99. Triethylene glycol is the only exception. The variation of $D_{AB}\eta$ is slightly larger than those of D_{AB} and .

SEMIEMPIRICAL CORRELATION OF DIFFUSIVITY

In Table 16 the experimental values for diffusivities of the glycols into water and of water into glycols are given together with those calculated from the correlations of Wilke-Chang (19), Othmer and Thakar (20) and Siraraman, Ibrahim and Kuloor (21). In general, for diffusion of water into glycols, the values calculated from the Wilke-Chang correlation agree with the experimental data better than those from Othmer and Kuloor. All of the predicted values except those for triethylene glycol were less than the experimental ones.

For diffusion of glycols into water, all the estimated values agree very poorly with the experimental results. The agreement between the three correlations is fairly good considering the different assumptions made in their derivation. Despite the good agreement of the three correlations, the experimental results are far higher than the predicted values. A reason for this will be given later.

Although the Wilke-Chang correlation gave the best prediction for the diethylene glycol-water system as discussed in Chapter V, it is worth giving a detailed discussion for ethylene and triethylene glycol systems (2). Adopting X = 1 for the diffusion of water into glycol and X = 2.6 for the diffusion of glycols into water, the Wilke-Chang correlation can be expressed as

Table 16.

Experimental and Calculated Values of Diffusivity of the Infinitely Dilute Glycol-Water Systems at 25 °C

Solute (Minor Component)	Solvent (Major Component)	$D_{AB} \times 10^6$ cm^2/sec Exp.*	$D_{AB} \times 10^6$ cm^2/sec Wilke-Chang+	Deviation %	$D_{AB} \times 10^6$ cm^2/sec Othmer-Thaker	Deviation %	$D_{AB} \times 10^6$ cm^2/sec Kuloor et al	Deviation %
Ethylene glycol	Water	27.	13.8	48.89	12.74	52.87	10.74	62.70
Water	Ethylene glycol	2.10	1.796 (2.196X = 1.5)	16.93	0.955	54.52	1.215	42.14
Diethylene glycol	Water	28.0	9.66	65.5	9.03	67.75	10.18	63.64
Water	Diethylene glycol	1.4	1.38	1.43	0.752	46.28	0.734	47.57
Triethylene glycol	Water	36.4	7.754	78.7	7.25	80.08	6.21	82.9
Water	Triethylene glycol	1.00	1.255	25.5	0.332	66.8	0.702	29.8

* Extrapolated values

$$\text{Deviation} = \frac{D_{AB}\text{Cal.} - D_{AB}\text{exp.}}{D_{AB}\text{exp.}} \times 100$$

+ Using X = 1 and 2.6

$$D_{AB} = 7.4 \times 10^{-8} \quad \frac{(M)^{\frac{1}{2}} T}{V^{0.6} \eta} \tag{4}$$

for water into glycol

and

$$D_{AB} = 11.9 \times 10^{-8} \quad \frac{(M)^{\frac{1}{2}} T}{V^{0.6} \eta} \tag{5}$$

for glycol into water.

The results are plotted in Figures 35, 36, and 37 together with observed values. For ethylene glycol and triethylene glycol-water systems with water as the solute, the estimated values are lower than the experimental results. But when X, the association parameter, was changed from 1 to 1.5 as done by Reed and Sherwood (38), the deviations never exceeded 15% even for concentrations from 100% down to 50 wt. % of ethylene glycol. There is a large deviation for the triethylene glycol-water system especially for the first two points. For the diffusion of glycol into water the use of the factor 2.6 as recommended by Wilke and Chang for systems with water as solvent, gives predicted values far less than the observed diffusivities. If one adopts X = 11 for ethylene glycol and X = 56 for triethylene glycol the correlation can be greatly improved.

Figure 38 shows diffusivities of the glycol-water systems, both for cases of glycols diffusing into water and for water diffusing into glycols at infinite dilution, plotted against the numbers of carbon atoms of the glycols. For water diffusing into glycols, diffusivities decrease as the carbon chain lengthens, while for glycols diffusing into water, the diffusivities increase as the number of carbon atoms increase.

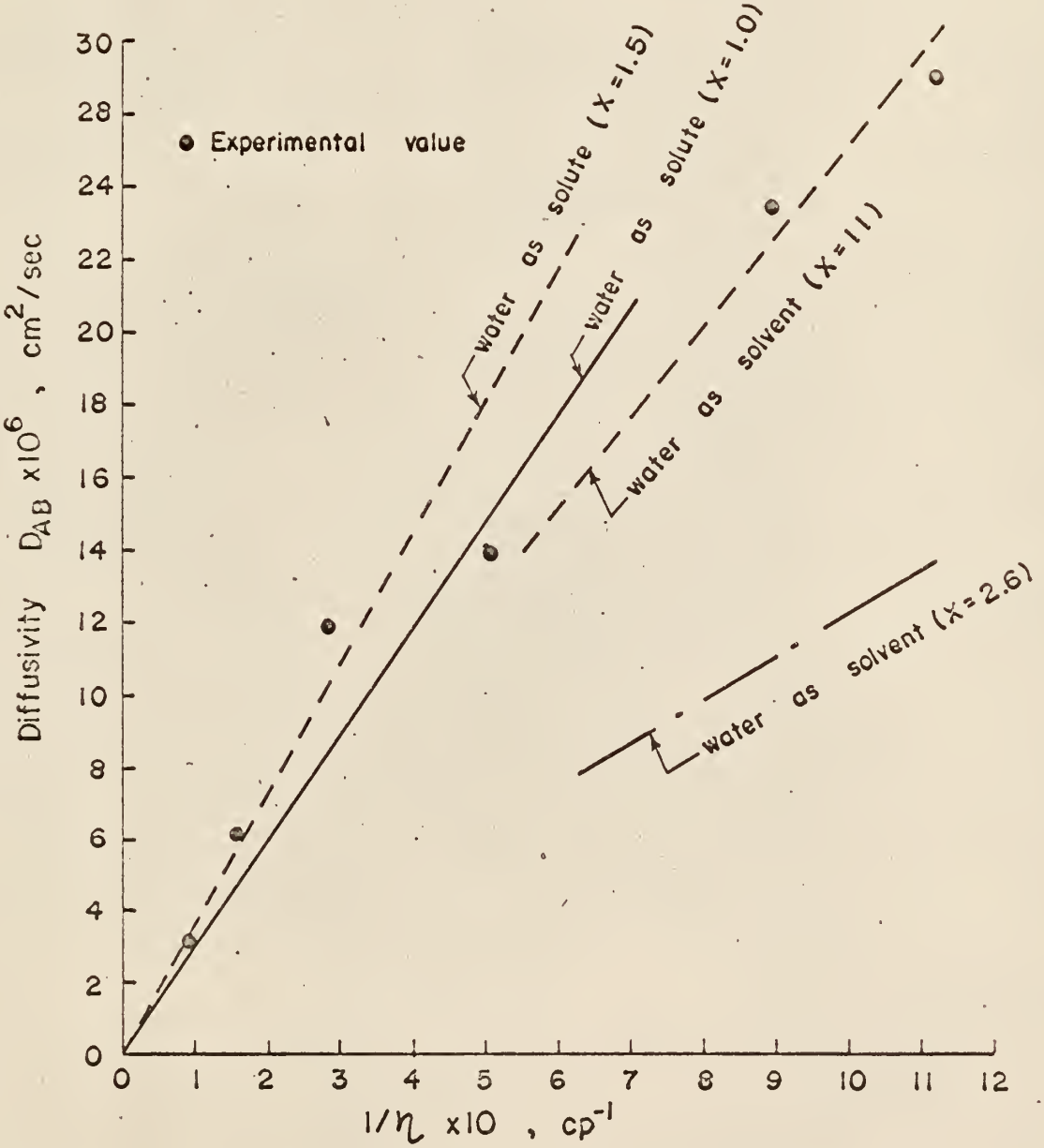


Fig. 35 . Plot of the Wilke-Chang correlation for the ethylene glycol-water system .

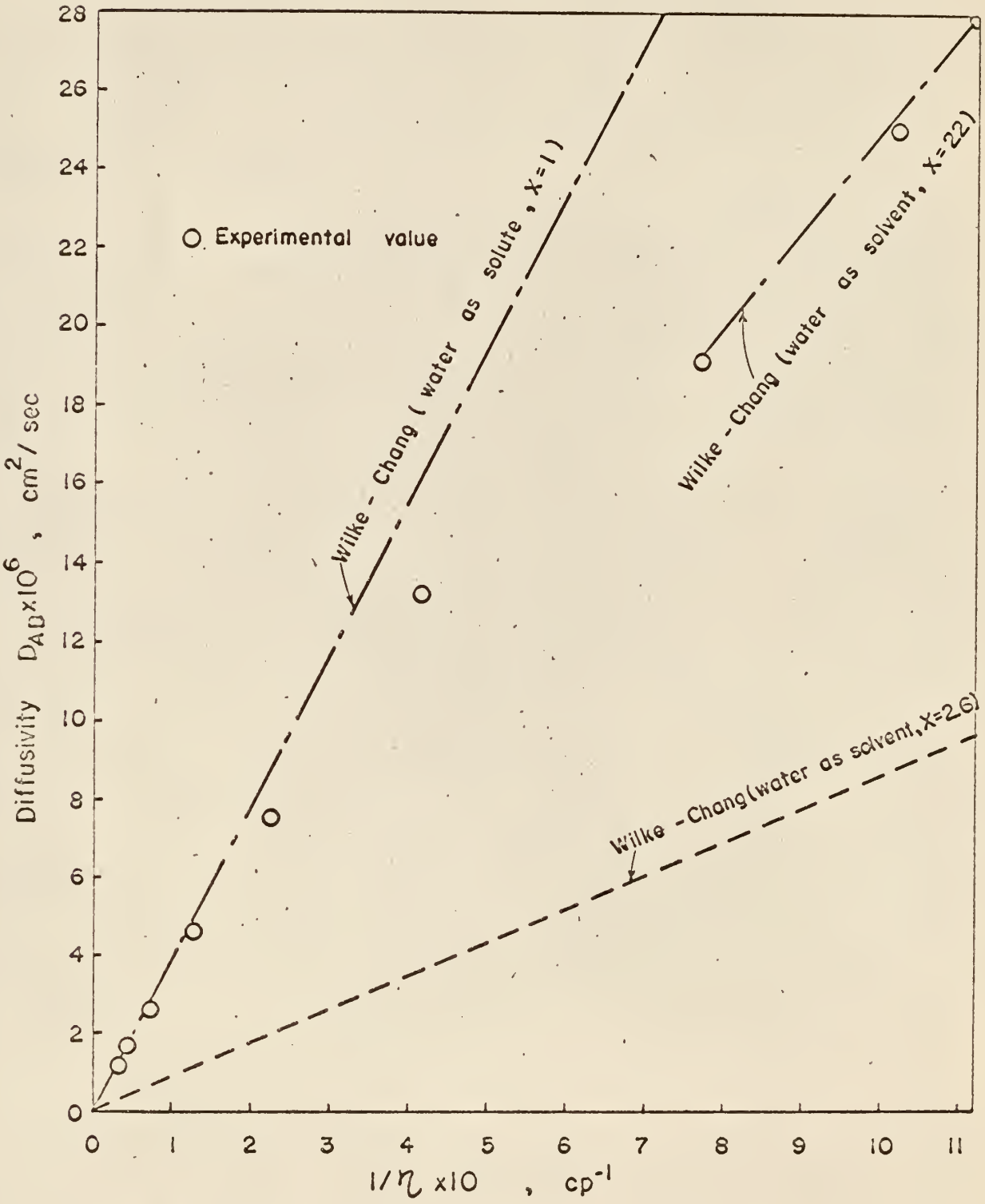


Fig. 36. Plot of the Wilke-Chang correlation for the diethylene glycol-water system at 25°C.

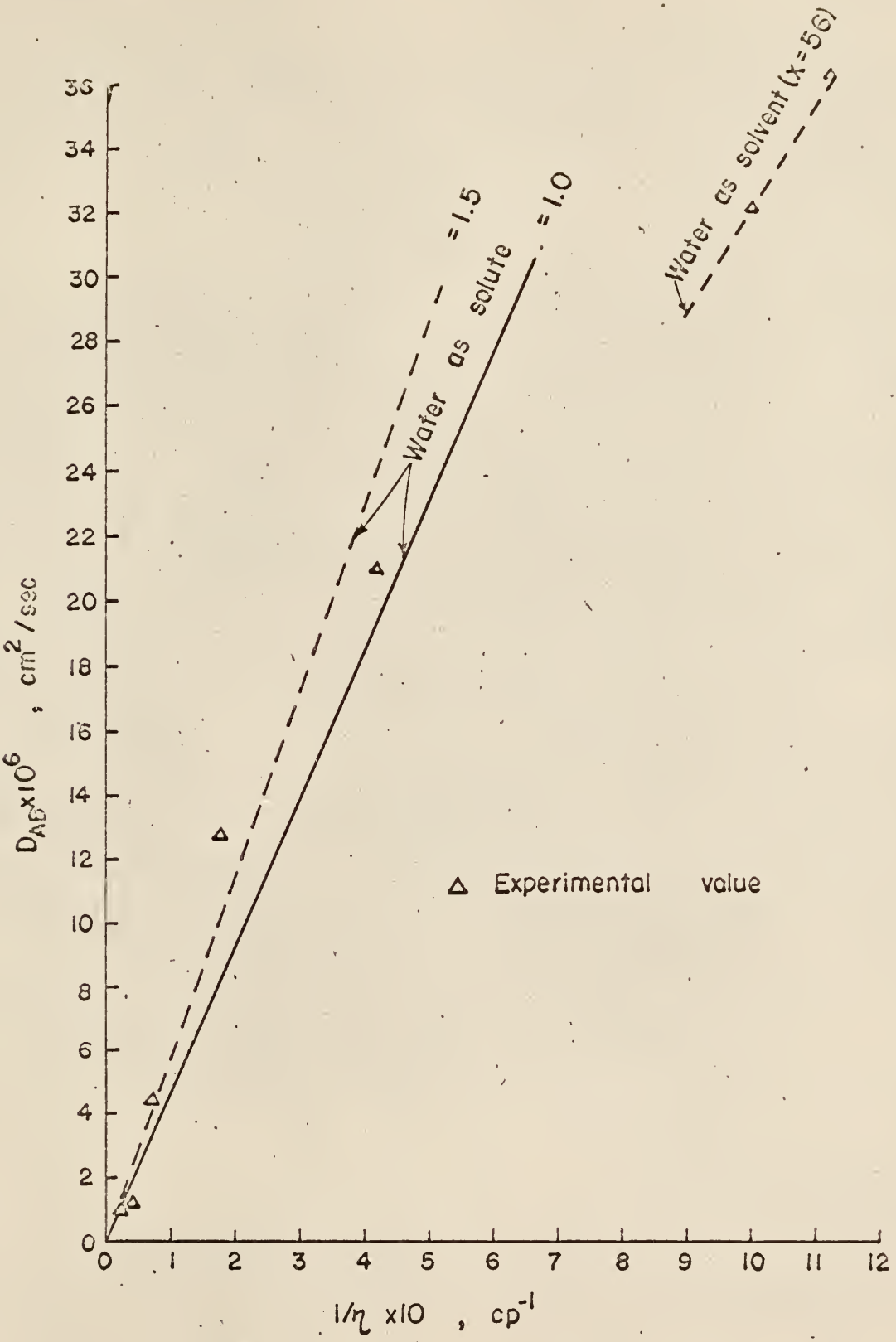


Fig. 37. Plot of the Wilke-Chang correlation for the triethylene glycol-water system.

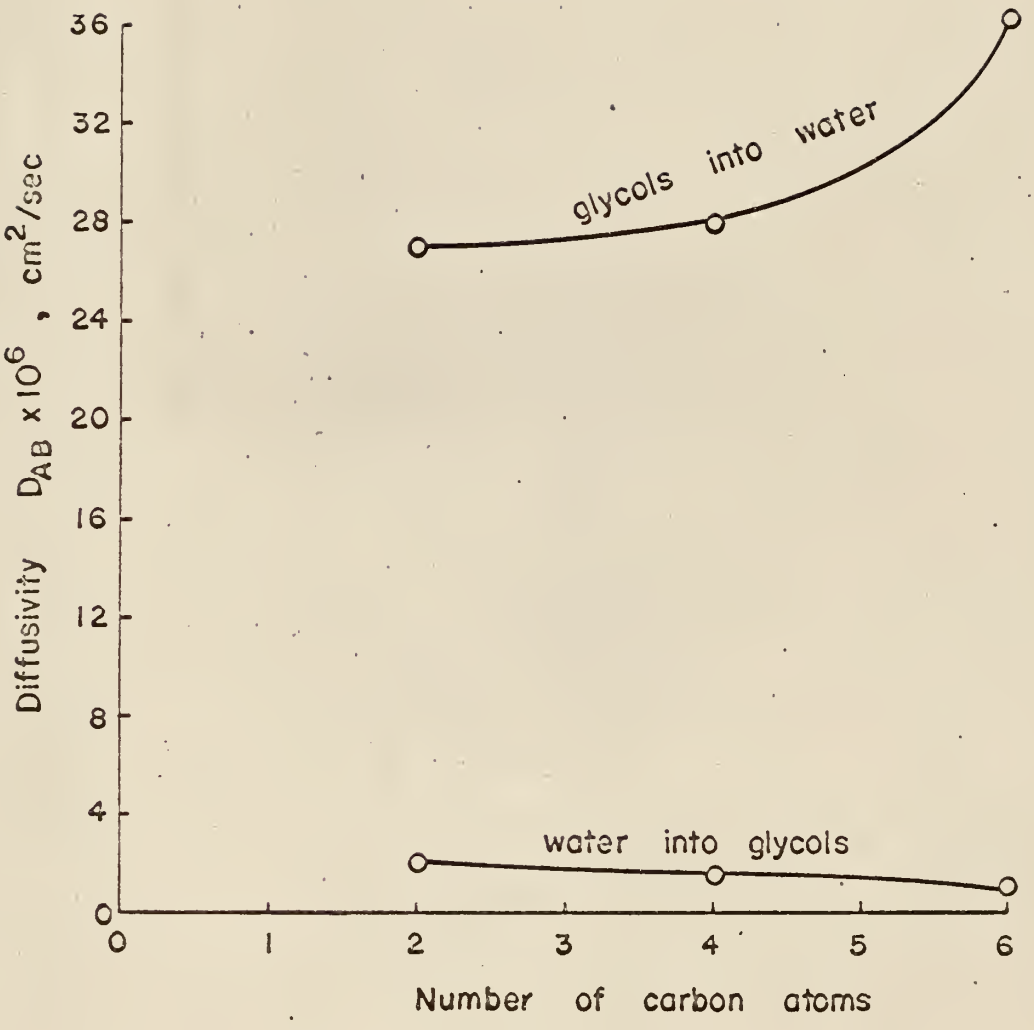


Fig. 38. Diffusivities of glycols and water.

COMPARISON WITH OTHER RESULTS

Garner and Merchant (39) investigated the diffusivity of the ethylene glycol-water system by using a Zeiss diffusion interferometer. Konnecke, Pechstein and Zobelt (42) also measured the same system at 20, 30 and 40 ^{o}C. Recently, Byers and King (43) reexamined the system by using diaphragm cells and the differential interferometer. The results of their works are shown in Figure 39 together with works done by Jerome (2). All these workers employed different systems in measuring the diffusivity. Byers and King stated that their results at 25 ^{o}C agreed with those of Garner and Merchant to better than 5% (43). In the high concentration range, the data of Konnecke et al. are considerably higher than others and Jerome's results fall between those by Konnecke et al. and those by Byers and King as can be seen from Figure 39. At the low concentration end, Jerome's data are the highest among all sets of the data and almost twice as high as those of Byers and King.

CONCLUSION AND RECOMMENDATION

The results of the experimental work shows that the diffusivities of aqueous glycol solutions are very concentration dependent. It is incorrect to assume them to be constant for a wide concentration range.

Examination of the data (listed in the Appendix) obtained at a low concentration range of glycols shows that the agreement between each run at the same concentration of the same solution is poorer than that of those at high concentration. The data for the ethylene glycol-water system obtained by Jerome at the lower concentration range of ethylene glycol deviate considerably from those by others. The experimentally measured diffusivities of glycols diffusing through water at infinite

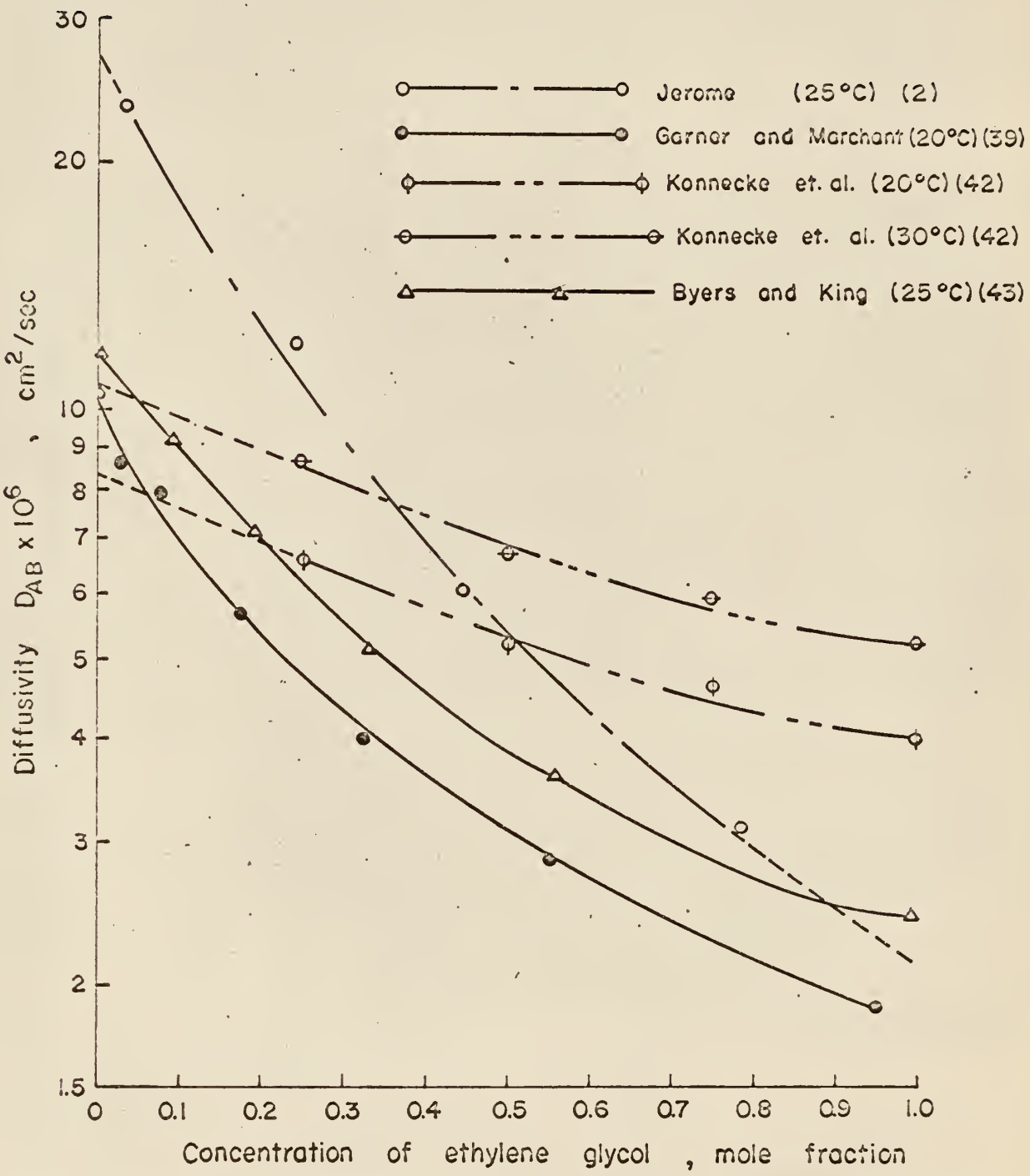


Fig.39. Diffusivity of ethylene glycol-water system by several workers .

glycol dilution are considerably different from those calculated using the empirical correlations. All these facts appear to indicate that the data obtained by using the microinterferometric method at the low concentration of glycols are not very reliable. When the concentration of a glycol in the solution is low, its viscosity is also generally low and the bulk mixing effect caused by the initial contact velocity becomes very appreciable and this would give rise to an abnormally high value of the measured diffusivity. To visualize the existence of the bulk mixing effect, consider two limiting cases, non-viscous or inviscid fluids and infinitely viscous fluids (i.e., solid). For non-viscous or inviscid fluids, the bulk flow caused by the initial contact velocity would continue indefinitely, whereas mixing would be negligible for infinitely viscous fluids (a solid). The use of the diffusivity of a glycol-water system obtained by the microinterferometric method when the concentration of a glycol is very low is not recommended. The lowest limit appears to be approximately where a drastic change of viscosity occurs. Actually the greatest advantage of the microinterferometric method is achieved when it is employed in measuring diffusivities of highly viscous materials such as polymer solutions (30, 44). To measure the diffusivities of a component in any system in the whole concentration range, it is desirable to use other devices when the viscosity of solution becomes low. Investigation of the temperature effect is also recommended.

NOMENCLATURE

Symbols

a_A	Activity of the solute
$\bar{C}$	Average concentration
C_A	Concentration of component A
C_{Ao}', C_{Ao}''	Initial concentrations of two different solutions
D_{AB}	Binary diffusion coefficient
D_{AB}^o	Ideal mutual diffusivity
D_B^o	Mutual diffusivity in an infinitely dilute solution of B in A
$E_{D,AB}$	Activation energy for the diffusion process
$E_{,B}$	Energy to overcome viscosity energy barrier
$g^{(2)}(\sigma)$	Correlation function
J_A	Flux of component A
k	Boltzman constant
L	Internal energy of the liquid
M	Molecular weight
M_{AB}	Mobility of solute molecule A through a stationary continum of species B
N	Avogadro's number
n	Refractive index
n_o', n_o''	Refractive indices of two different solutions
P	Pressure
R	Gas constant
r_A	Molecular radius
V_A	Molal volume of the diffusion substance

NOMENCLATURE--Continued

Symbols

T	Temperature
X	Association parameter
X_A	Mole fraction of component A
η	Viscosity of the solution
η_B	Viscosity of the solvent
η_W	Viscosity of water
ϕ_A	The solute volume fraction
ζ	Arbitrary packing parameter

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to his major advisor, Dr. L. T. Fan, for his constant advice and guidance in this study. The author also expresses his gratitude to Professor R. G. Akins for his helpful suggestions and to Dr. F. S. Jerome for his assistance. The financial support of this work from Kansas State University Engineering Experiment Station project 2346 and from the NSF Grant GK67 are also acknowledged.

BIBLIOGRAPHY

1. Nishijima, Y., and G. Oster, J. of Chem. Education. 38, 144 (1961)
2. Jerome, F. S., Ph.D. Thesis. Kansas State University (1967)
3. Fick, A., Pogg. Ann. 94, 59 (1855)
4. Graham, T., Phil. Mag. 151, 183 (1861)
5. Bird, R. B., W. E. Stewart and E. N. Lightfoot, "Transport Phenomena", John Wiley and Sons, New York (1960)
6. Geddes, A. L., and R. B. Pontius, "Physical Method" Part II, Chapter XVI. Interscience Publishers, New York (1960)
7. Boltzmann, L., Ann. Physik, 53, 959 (1894)
8. Einstein, A., Ann. Physik, 17, 549 (1905); 19, 289 (1906); 34, 591 (1911)
9. Smoluchowski, M. V., Ann. Physik, 21, 756 (1906)
10. Kuhn, W., Kuhn, H., and P. Bucher, Ergebn. exakt. Naturwiss, 25, 1, Springer-Verlag, Berlin (1951)
11. Pyun, C. N., and M. Fixman, J. Chem. Phys., 41, 937 (1964)
12. Glasstone, S., K. J. Laidler, and H. Eyring, "The Theory of Rate Processes". McGraw-Hill, New York (1941)
13. Gainer, J. L., and A. B. Metzner, A. I. Ch. E.-I. Ch. E. Symposium Series No. 6, (1965)
14. Rice, S. A., J. Chem. Phys., 31, 584 (1959)
15. Rice, S. A., et al., J. Chem. Phys. 31, 575 (1959)
16. Rice, S.A., and J. G. Kirkwood, J. Chem. Phys., 31, 901 (1959)
17. Kamal, M. R., and L. N. Canjar, Chem. Eng. Progress, 62, 82 (1966)
18. Wilke, C. R., Chem. Eng. Progr., 45, 218 (1949)
19. Wilke, C. R., and P. Chang, A. I. Ch. E. J., 1, 264 (1955)
20. Thakar, N. S., and D. F. Othmer, I. & E. C., 45, 589 (1953)
21. Sitaraman, R., S. H. Ibrahim, and N. R. Kuloor, J. Chem. Eng. Data, 8, 198 (1965)

BIBLIOGRAPHY--Continued

22. Cadwell, C. S., and A. L. Babb, J. Phys. Chem., 60, 51 (1956)

23. Dullin, F. A. L., and L. W. Shemilt, Nature, 190, 526 (1961)

24. Kamal, M. R., and L. N. Canjar, A. I. Ch. E. J., 8, 329 (1962)

25. Lisnyanski, L. I., and M. F. Vuks, Russian J. Phys. Chem., 38, 339 (1964)

26. Rathbum, R. E., and A. L. Babb, Private Communication

27. Fürth, R., Physik Z., 26, 719 (1925)

28. Berg, W. F., Proc. Royl. Soc. London, A164, 79 (1938)

29. Searle, F. C., Phil. Mag., 37, 316 (1946)

30. Nishijima, Y., and G. Oster, J. Polymer Science, 19, 337 (1956)

31. Eckert, J. E., and F. R. Shaw, "Beekeeping", The Macmillan Co., New York (1960)

32. Gladden, J. K., and M. Dole, J. Amer. Chem. Soc., 75, 3900 (1953)

33. Vignes, A., I. & E. C. Fundamental, 5, 189 (1966)

34. Eucken, A., Lehrbuch II, 2, 1065. Akad. Verl. Ges., Leipzig (1949)

35. MaCall, P. W., and E. W. Anderson, J. Phys. Chem., 70, 601 (1966)

36. Standinger, H., "Die hochmolekularen organischen verbindungen", Berlin, J. Springer, (1932)

37. Curme, G. O., Ed. "Glycols", Reinhold Publishing Corp., New York (1952)

38. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill, New York (1966)

39. Garner, F. H., and P. J. M. Marchant, Trans. Instn. Chem. Engrs., 39, 397 (1961)

40. "Glycols, Properties and Uses", The Dow Chem. Co. (1956)

41. Cragoe, C. S., "Properties of Ethylene Glycol and Its Aqueous Solutions", Washington D. C., National Bureau of Standard.

42. Konnecke, H. G., Pechstein, G., and R. Zobelt, Z. Physik Chem.

BIBLIOGRAPHY--Continued

43. Byers, C. H., and C. J. King, J. Phys. Chem., 70, 2499 (1966)

44. Secor, R. M., A. I. Ch. E. J., 11, 452 (1965)

APPENDIX

Table A I-1

Summary of Experimental Diffusivity
for Honey-Water System at 25 °C

Co' = 65.41, Co" = 74.92, $\overline{C}$ = 70.16 (wt. % Honey)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^{6}$ cm^2/sec
4	13-16	3.58
13	42-44	1.55
14	45-48	1.94
15	49-52	4.12
16	53-55	2.63

Table A I-2

Summary of Experimental Diffusivity
for Honey-Water System at 25 °C

Co' = 74.92, Co" = 85.94, $\overline{C}$ = 80.43 (wt. % Honey)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
5	17-19	2.48
7	24-27	1.64
8	28-30	1.51
18	60-63	0.866

Table A I-3

Summary of Experimental Diffusivity
for Honey-Water System at 25 °C

Co' = 85.94, Co" = 100, $\overline{C}$ = 92.97 (wt. % Honey)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^7$ cm^2/sec
9	31-32	1.67
10	33-35	1.32
11	36-38	1.33
12	39-41	1.63

Table A I-4

Summary of Experimental Diffusivity
for Honey-Water System at 25 ^{o}C

Co' = 93.51, Co" = 100, $\overline{C}$ = 96.75 (wt. % Honey)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^{7}$ cm^2/sec
19	64-66	1.35
20	67-71	1.10
21	72-77	1.43

Table AII-1.

Summary of Experimental Diffusivity for Diethylene Glycol-Water System at 25 °C

Co' = 100, Co" = 86.47, $\bar{C}$ = 93.23 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
1	1-4	1.64
2	5-8	1.99
3	9-12	1.27
4	13-16	1.84

Table AII-2.

Summary of Experimental Diffusivity for Diethylene Glycol-Water System at 25 °C

Co' = 86.47, Co" = 72.23, $\overline{C}$ = 79.35 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
5	17-20	2.33
6	21-23	3.00
7	24-27	2.06
8	28-31	2.25

Table AII-3.

Summary of Experimental Diffusivity for Diethylene Glycol-Water System at 25 °C

Co' = 72.23, Co" = 56.85, $\overline{C}$ = 64.54 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
9	32-35	5.34
10	36-39	4.86
11	40-43	3.95
12	44-47	4.30

Table AII-4.

Summary of Experimental Diffusivity for Diethylene Glycol-Water System at 25 °C

$Co' = 56.85$, $Co'' = 43.08$, $\bar{C} = 49.96$ (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
13	48-51	5.51
14	52-55	10.3
15	56-59	6.62
16	60-63	4.63
27	104-107	8.21
28	108-111	9.96

Table AII-5.

Summary of Experimental Diffusivity for Diethylene Glycol-Water System at 25 °C

Co' = 43.08, Co" = 26.96, $\overline{C}$ = 35.02 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
18	64-67	9.6
32	120-123	13.3
33	124-127	16.6

Table AII-6.

Summary of Experimental Diffusivity for Diethylene Glycol-Water System at 25 °C

Co' = 26.96, Co" = 11.25, $\overline{C}$ = 19.10 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
19	72-75	19.4
21	80-83	19.3
22	84-87	18.7

Table AII-7

Summary of Experimental Diffusivity for Diethylene Glycol-Water System at 25 °C

Co' = 11.25, Co" = 0.0, $\overline{C}$ = 5.62 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
23	88-91	25.2
24	92-95	20.9
25	96-99	28.8

Table A III-1.

Summary of Experimental Diffusivity for Polyethylene Glycol-Water System at 25°C

Co'== 100, Co" = 86.44, $\bar{C}$ = 93.22 (wt. % glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
22	78-81	0.712
23	82-85	0.721
24	86-89	0.770
25	90-93	0.758

Table A III-2.

Summary of Experimental Diffusivity for Polyethylene Glycol-Water System at 25 °C

Co' = 86.44, Co" = 72.10, $\overline{C}$ = 79.27 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
26	94-97	0.862
27	98-101	0.853
28	102-105	0.815
29	106-109	0.865

Table A III-3.

Summary of Experimental Diffusivity for
Polyethylene Glycol-Water System at 25 °C

Co' = 72.10, Co" = 57.50, $\overline{C}$ = 64.80 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
30	110-113	2.78
31	114-117	2.20
32	118-121	1.89
33	122-125	1.98

Table A III-4.

Summary of Experimental Diffusivity for
Polyethylene Glycol-Water System at 25 °C

$Co' = 57.50$, $Co'' = 42.25$, $\bar{C} = 49.87$ (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
34	126-129	3.59
35	130-133	3.74
36	134-137	4.01

Table A III-5.

Summary of Experimental Diffusivity for
Polyethylene Glycol-Water System at 25 °C

Co' = 42.25, Co" = 26.89, $\overline{C}$ = 34.57 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
42	178-180	12.7
48	197-200	11.0

Table A III-6.

Summary of Experimental Diffusivity for Polyethylene Glycol-Water System at 25 °C

Co' = 26.89, Co" = 11.18, $\overline{C}$ = 19.03 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
43	181-183	23.8
44	184-185	21.8

Table A III-7.

Summary of Experimental Diffusivity for Polyethylene Glycol-Water System at 25 °C

Co' = 11.18, Co" = 0.0, $\overline{C}$ = 5.59 (wt. % Glycol)

Run Number	Plate Number	Diffusivity $D_{AB} \times 10^6$ cm^2/sec
55	225-228	46.9
57	233-236	43.0

MEASUREMENTS OF LIQUID PHASE DIFFUSION BY THE MICROINTERFEROMETRIC METHOD

by

JIE-TSAI TSENG

B.S., National Taiwan University, 1964

Taipei, Taiwan

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1968

ABSTRACT

Binary diffusivities of honey-water, diethylene glycol-water and polyethylene glycol-water systems were experimentally measured at 25 ^{o}C by the microinterferometric method. Refractive indices and viscosities were also determined. The experimental diffusivities of three glycol-water systems, i.e., ethylene glycol-water, diethylene glycol-water, and triethylene glycol-water, were compared with those calculated from several empirical correlations. It was found that at high concentration of glycols the Wilke-Chang correlation gave the best predicted values.

The microinterferometric method is very convenient in measuring the diffusivities of highly viscous materials. When the viscosity of the solution becomes low it was found that the method was not very suitable. The use of other devices is recommended to measure the diffusivities of less viscous liquids.